

Materials for Ultra Supercritical Fossil Power Plants

TR-114750

Final Report, March 2000

Effective December 6, 2006, this report has been made publicly available in accordance with Section 734.3(b)(3) and published in accordance with Section 734.7 of the U.S. Export Administration Regulations. As a result of this publication, this report is subject to only copyright protection and does not require any license agreement from EPRI. This notice supersedes the export control restrictions and any proprietary licensed material notices embedded in the document prior to publication.

EPRI Project Managers
R. Viswanathan
W. T. Bakker

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Electric Power Research Institute, Inc. (EPRI)

ORDERING INFORMATION

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (800) 313-3774.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

Copyright © 2000 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

EPRI
3412 Hillview Avenue
Palo Alto, California 94304

Principal Investigators
R. Viswanathan
W. T. Bakker

This report describes research sponsored by EPRI.

The report is a corporate document that should be cited in the literature in the following manner:

Materials for Ultra Supercritical Fossil Power Plants, EPRI, Palo Alto, CA: 2000. TR-114750.

REPORT SUMMARY

Ultra supercritical fossil power plants are under development worldwide to improve efficiency and reduce CO₂ emissions. Material development and selection are critical to the success of these efforts. This report provides a critical review of available and developmental materials.

Background

The efficiency of conventional boiler/steam turbine fossil power plants is a strong function of the steam temperature and pressure. Since the energy crisis in the 1970s, research to increase both has been pursued worldwide. The need to reduce CO₂ emission has recently provided an additional incentive to increase efficiency. Thus, steam temperatures of the most efficient fossil power plants are now in the 600°C range, which represents an increase of about 60°C in 30 years. It is expected that steam temperatures will rise another 50-100°C in the next 30 years. The main enabling technology for this development is the advent of stronger high temperature steels, capable of operating under high stresses at ever increasing temperatures. This report provides the present state of the art and technical background of this development effort.

Objective

To provide a state-of-the-art review of materials for advanced boiler/steam turbine power plants (ultra supercritical power plants).

Approach

The authors critically reviewed all available information from the open literature consisting of EPRI- sponsored projects and collaborative research projects. The two main areas of concern were materials developments for boilers and for steam turbines. In the boiler area the authors emphasized materials for thick section components such as steam headers and piping, material for reheater and super-piping, and waterwall materials. In the turbine area special attention was given to turbine rotor and blade materials.

Results

High strength ferritic 9-12Cr steels for use in thick section components are now commercially available for temperatures up to 620°C. Field tests are in progress, but long-term performance data are not yet available.

Initial data on two experimental 12Cr ferritic steels indicate that they may be capable of long-term service up to 650°C, but more data are required to confirm this.

Advanced austenitic stainless steels for reheater and super-tubing are available for service temperatures up to 650°C and possibly 700°C. None of these steels have been approved by the ASME Boiler Code Group so far.

Higher strength materials are needed for upper water construction of plants with steam pressures above 24 MPa. A high strength 2-1/2%Cr steel recently ASME Code approved as T-23 is the preferred candidate material for this application. Field trials are in progress.

Steam turbine rotors for service up to 650°C have been successfully manufactured. Their suitability for long-term service, especially at the higher temperatures, remains to be determined.

EPRI Perspective

Worldwide efforts to increase efficiency and reduce CO₂ emissions of conventional boiler/steam turbine have grown and will likely continue to do so in the foreseeable future. EPRI participated in the critical materials developments needed to make such plants viable and intends to continue the efforts in collaboration with its worldwide partners.

TR-114750

Keywords

Boilers

Steam turbines

Ultra supercritical steam systems

Ferritic steels

Austenitic steels

CONTENTS

1 INTRODUCTION AND BACKGROUND	1-1
2 BOILER MATERIALS REQUIREMENTS	2-1
2.1 Historical Evolution of Steels	2-2
2.2 Development Philosophy for Ferritic Steels, Mainly for Use in Thick Section Piping	2-3
2.3 Development Philosophy for Austenitic Steels, Mainly for Superheater Tubing	2-5
2.4 Choice of Materials for Headers and Steam Pipes	2-9
2.5 Choice of Materials for Superheater/Reheater Tubes	2-15
2.5.1 Creep Rupture Strength	2-15
2.5.2 Fire-side Corrosion	2-17
2.5.3 Steam-side Oxidation	2-21
2.5.4 Summary of Tube-Material Status	2-22
2.6 Choice of Materials for Waterwalls	2-23
2.6.1 Metal Temperature Concerns	2-23
2.6.2 Waterwall Corrosion Concerns	2-23
3 STEAM TURBINE MATERIALS	3-1
3.1 HP/IP Rotors	3-1
4 BLADE MATERIALS	4-1
5 BOLTING MATERIALS	5-1
6 CONCLUSIONS	6-1
7 REFERENCES	7-1

LIST OF FIGURES

Figure 1-1 Improvements in heat rate (efficiency) achieved by increasing steam temperature and pressure using single and double reheat cycles (Ref. 2), compared to the base case of 535°C/18.5 MPa	1-2
Figure 1-2 International R&D programs for advanced supercritical plant (Ref. 1)	1-6
Figure 2-1 Historic evolution of materials in terms of increasing creep rupture strength (8).....	2-3
Figure 2-2 Evolution of ferritic steels for boilers (8).....	2-4
Figure 2-3 Evaluation of authentic steels for boilers (8).....	2-6
Figure 2-4 Comparison of allowable stresses of ferritic steels for boiler (8)	2-11
Figure 2-5 Comparison of allowable stresses and sectional view of main steam pipes designed at 570°C and 600°C (15)	2-13
Figure 2-6 Cost of P-22, P-91 and P-122 steels header materials as a function of temperature at 31 Mpa steam pressure (15).....	2-13
Figure 2-7 Comparison of allowable stresses for 18Cr-8Ni and 15Cr steels (Ref. 17)	2-16
Figure 2-8 Comparison of allowable stresses for austenitic alloys containing more than 20% Cr (based on Ref. 17)	2-16
Figure 2-9 Allowable metal temperatures at constant allowable stress of 49 Mpa (7 ksi) as a function of chromium content for various alloys (Ref. 17).....	2-17
Figure 2-10 Relationship between hot-corrosion weight loss and temperature for ferritic steels (18)	2-18
Figure 2-11 Relationship between hot-corrosion weight loss and chromium content for various alloys (19)	2-18
Figure 2-12 Comparison of fire-side corrosion resistance of various alloys (20)	2-19
Figure 2-13 Metal losses of various superheater steels in a boiler using bituminous eastern U.S. coals (23).....	2-20
Figure 2-14 Metal losses of various superheater steels in a boiler subbituminous western U.S. coals (23).....	2-21
Figure 2-15 Corrosion of steels containing 0.5-18% Cr under FeS containing deposits in oxidizing flue gas	2-24
Figure 3-1 Evolution of HP/IP steam turbine rotor alloy showing compositional changes and increasing temperature capability	3-2
Figure 3-2 Larson-Miller rupture curves for commercial and developmental 12% Cr rotor steels.....	3-4
Figure 3-3 Fracture toughness of turbine rotor steels (1).....	3-4

Figure 4-1 Stress rupture properties of candidate super alloys for bucket (based on Ref. 45).....	4-3
---	-----

LIST OF TABLES

Table 1-1 Most Recent Large-Scale Coal-Fired Power Plants in Japan Utilizing 593°C Steam (Based on Ref. 5)	1-4
Table 1-2 Recent Large Scale Coal Power Plants in Germany and Denmark (based on Refs. 2 and 6).....	1-5
Table 2-1 Nominal Chemical Compositions of Ferritic Steels for Boilers	2-7
Table 2-2 Nominal Chemical Compositions of Austenitic Steels for Boiler (wt%).....	2-8
Table 2-3 Candidate Materials for Advanced Supercritical Plants for Various Steam Conditions	2-12
Table 2-4 Application of New Tungsten-Bearing Steels in European Power Stations (Ref. 6).....	2-14
Table 3-1 Candidate Materials for Advanced Steam Turbines.....	3-1
Table 3-2 Nominal Chemical Compositions of Candidate Alloys for High Temperature Rotors	3-5
Table 4-1 Nominal Chemical Compositions of Candidate Alloys for Buckets (WT%).....	4-2
Table 4-2 Features and Problems of Four Candidate Alloys for Blades.....	4-5
Table 5-1 Chemical Composition of Superalloy Bolt Materials in Steam Turbines (37), (46).....	5-1
Table 5-2 Failure of Superalloy Bolt Materials in Steam Turbines (37), (46).....	5-2

1

INTRODUCTION AND BACKGROUND

Improvements in the efficiency of pulverized coal (P.C.) fired boiler/steam turbine power plants have been pursued since the introduction of P.C. fired boilers in the 1920's. This led eventually in the late 1960's to the introduction of supercritical boilers operating at about 570°C (1060°F) superheat/reheat temperatures and 24 MPa (3400 psi) pressure for the steam. Due to initial operating difficulties, efficiencies then decreased, at least in the USA, and most utilities reverted to subcritical units with steam conditions of about 535°C/17 MPa (1000°F/2400 psi). The main steam temperature was standardized throughout the world around 540°C (1000°F), although 565°C (1050°F) has for many years been the standard for coal-fired plants in Europe, particularly in the UK, with the main steam pressure being 18.5 MPa (2600 psi).

The energy crisis in mid 70s and subsequent sharp increase in fuel prices re-kindled interest in the development of more efficient P.C. power stations. An improvement in thermal efficiency of the plant not only reduces the fuel costs but also reduces the release of SO₂, NO_x and CO₂ emissions. The latter is very significant in view of the world-wide agreements to reduce CO₂ emissions by 2010 and the fact that a 1% increase in efficiency of an 800 MW machine would lead to a life-time reduction in CO₂ approaching one million tonnes⁽¹⁾.

Figure 1-1 illustrates the improvements in heat rate that can be achieved by increasing steam temperature and pressure by use of advanced steam conditions⁽²⁾. For example, using a 538°C/18.5 MPa (1000°F/2600 psi) steam plant as a base case, a heat rate decrease of nearly 6% is achieved by changing the steam conditions to about 593°C/30 MPa (1100°F, 4300 psi). At 650°C (1200°F) the decrease in heat rate is as much as 8%. There has been some experience in Europe in the chemical industry where numerous low power rating (3 to 125 MW) plants operating at steam temperatures of 600°C (1112°F) and 650°C (1200°F) and pressures of 18 MPa (2600 psi) and 33 MPa (4800 psi) were built in the 1950s and 60s⁽¹⁾. A large supercritical 375 MW plant was built in UK at Drakelow C.

In the United States, there has been substantial experience based on two high-efficiency ultra supercritical plants (USC) built in the 1950's. Philo 6, a 125-MW plant owned by the Ohio Power Company, has been operational since 1957 under design steam conditions of 31 MPa (4500 psi) and a 610/565/538°C (1150/1050/1000°F) double-reheat temperature cycle. Eddystone 1, owned by Philadelphia Electric Company, was designed to operate under steam conditions of 34.5 MPa (5000 psi) and 650/565/565°C (1200/1050/1050°F), and has been operational since 1959. The plant has operated under de-rated conditions of 32.4 MPa (4700 psi) and 605°C (1125°F) for most of its service life, because of mechanical and metallurgical problems. Most of the problems were due to the use of austenitic steels for heavy section components operating at high temperatures. These steels have low thermal conductivity and high thermal expansion resulting in high thermal stresses and fatigue cracking. These problems

temporarily dampened utility interest in building ultra supercritical plants and defined the need for high strength ferritic steels.

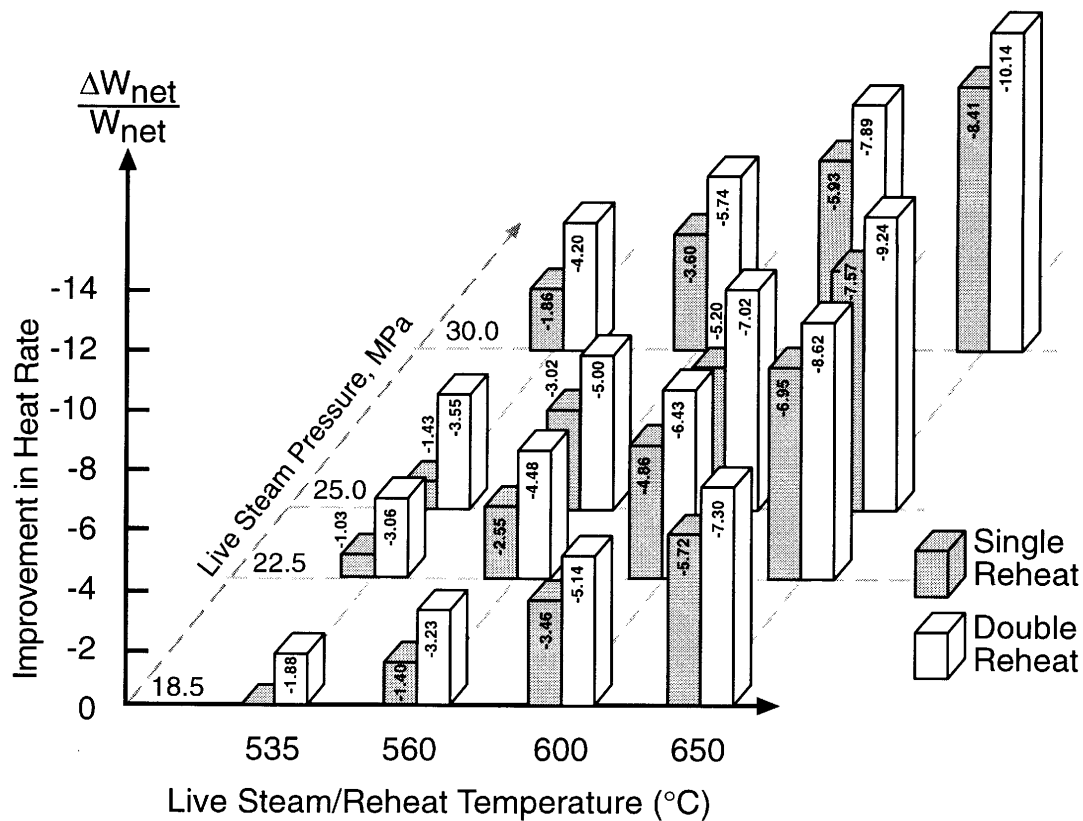


Figure 1-1
Improvements in heat rate (efficiency) achieved by increasing steam temperature and pressure using single and double reheat cycles (Ref. 2), compared to the base case of 535°C/18.5 MPa

EPRI initiated a study of the development of more economic coal-fired power plant in 1978^(3,4). This study re-awakened world-wide interest in advanced steam plants and resulted in a number of research and development studies involving US, Japanese and European manufacturers. These studies focused on developing further the existing high-temperature-resistant ferritic-martensitic 9%Cr and 12%CrMoV steels for the production of rotors, casings and chests, pipes and headers capable of operating at inlet steam temperatures of up to 650°C (1200°F). One of the early conclusions from this project was that the construction of a plant with a 593°C (1100°F)/31 MPa (4500 psi) steam condition would be feasible with only minor evolutionary improvements in materials technology. This has in fact proved to be correct as evidenced by the spate of power plants built in Japan and Europe over the last decade.

Table 1-1 is a list of the most recent large scale coal power plants in Japan⁽⁵⁾. Table 1-2 lists the recent coal power plants operating under advanced steam conditions in Germany and Denmark⁽⁶⁾. In general, the Japanese plants are larger in terms of rated output. The main steam and reheat steam temperatures are also higher, while the pressures are lower compared to the European

plants. The European plants seem to have standardized the main steam pressures around 30 MPa (4300 psi) compared to 24 MPa (3500 psi) for the Japanese plants. A major challenge in constructing USC plants has been in the area of materials technology. While materials suitable for metal temperatures up to 565°C (1050°F) were available, even 20 years ago, further developments were needed to achieve 593°C (1100°F) and beyond. Intense R&D efforts were carried out in Japan, USA and Europe as shown in Figure 1-2⁽¹⁾. In each case, a phased approach was adopted. For instance, in the USA, the following phases 0 to 2 were defined, where the temperatures given are for the main steam and first and second reheats.

Steam Conditions for coal-fired plants in EPRI program

EPRI	Pressure		Temperature	
<i>Program</i>				
Phase	Mpa	psig	°C	°F
0	310	4500	566/566/566	1050/1050/1050
1	310	4500	593/593/593	1100/1100/1100
1B	310	4200	620/620/620	1150/1150/1150
2	345	5000	649/649/649	1200/1200/1200

The Phase 0 conditions were considered to be achievable with the state-of-the-art technology in 1978 while the Phase 1 conditions were considered to be achievable with only minor improvements. The technology needed for phase 2 was considered well beyond reach and hence, an intermediate goal of 620-630°C (1150-1166)/30 MPa (4200 psi) seems to have been established in Europe and Japan. For convenience, this Phase will be referred to as 1B in this paper. Although the material developments for Phase 2 have not been fully achieved, technology exists today that will enable building plants that can meet Phase 1B conditions. This has been made possible by some very exciting progress in developing highly creep resistant 9 to 12%Cr ferritic steels. The objective of this report is to review developments in materials technology and to benchmark them against the goals set forth for the phased development of ultra supercritical coal power plants.

Introduction and Background

Table 1-1
Most Recent Large-Scale Coal-Fired Power Plants in Japan Utilizing 593°C Steam (Based on Ref. 5)

Power Plant	Electric Power Company	Rated Output MW	Main Steam Pressure MPa	Steam Temperature °C	Commissioning
Reihoku #1	Kyusyu	700	24.1	566/566	Jul-95
Noshino 2	Tohoku	600	24.1	566/593	1994
Haranomachi #1	Tohoku	1000	24.5	566/593	Jul-97
Matsuura #2	EPDC	1000	24.1	593/593	Jul-97
Nanao-Ohta #2	Hokuriku	740	24.1	593/593	Jul-98
Haranomaci #2	Tohoku	1000	24.5	600/600	Jul-98
Misumi #1	Tongoku	1000	24.5	600/600	Jul-98
Tachibana-wan	Kyusyu	700	24.1	566/593	Jul-00
Tachibana-wan #1	EPDC	1050	25	600/610	Jul-00
Tsuruga #2	Hokuriku	700	24.1	593/593	Oct-00
Reihoku #2	Kyusyu	700	24.1	593/593	Jul-00
Tachibana-wan #2	EPDC	1050	25	600/610	Jul-01
Hitachinaka 1	Tokyo Electric	1000	24.5	600/600	2002
Isogo 1	EPDC	1050	25	600/610	2002
Maizuni 1	Kansai	900	24.1	593/593	2003
Maizuni 2	Kansai	900	24.1	593/593	2003

Table 1-2
Recent Large Scale Coal Power Plants in Germany and Denmark (based on Refs. 2 and 6)

Power Station	Utility	Unit Size, MW	Main Steam °C/MPa	Hot Reheat °C/MPa	Efficiency %	Commissioning
Schkopau ⁽¹⁾	VKR	2x450	550/28.5	565/7.0	40.5	1995
Kirchmoser ⁽²⁾⁽³⁾	VKR	160	540/8.5	-	50	
Altbach ⁽²⁾⁽³⁾	Neckarwerke	330	545/28.5	568/7.5	42	
Schwarze Pumpe ⁽¹⁾	VEAG	2x800	552/28.4	570/6.6	40.5	1997/98
Nefo ⁽²⁾	Nordjyllands -vaerket	425	587/31.0	580/10.0	47	
Skaerbaek ⁽²⁾	Skaerbaek	425	587/31.0	580/10.0	47 ⁽⁴⁾	1997
Boxberg ⁽¹⁾	VEAG	2x>800	550/28.5	583/6.7	41	1998/99
Lippendorf ⁽¹⁾	VEAG	2x930	559/28.5	588/6.7	42	1999
Lubeck ⁽²⁾	PREAG	425	590/30.0	607/7.0	45.7	
Hebler ⁽²⁾	VKR	700	585/30.0	605/7.0	45	
Frimmersdorf ⁽¹⁾	RWE	950	585/28.6	605/7.0	43	
Bexbach ⁽²⁾	Saarberg	750	583/30.0	>78 bar	44	
Franken ⁽²⁾⁽³⁾	Bayernwerke	600/150	575/28.5	595/7.8	43	
Nordigland		400	583/29	580/-	48	1998
VKA (study)		500/900	605/27	625/	47	2002
RWE (study)		550	640/30	660	-	2004

(1) Lignite Coal, (2) Hard Coal, (3) combined Cycle, (4) Seawater Cooling.

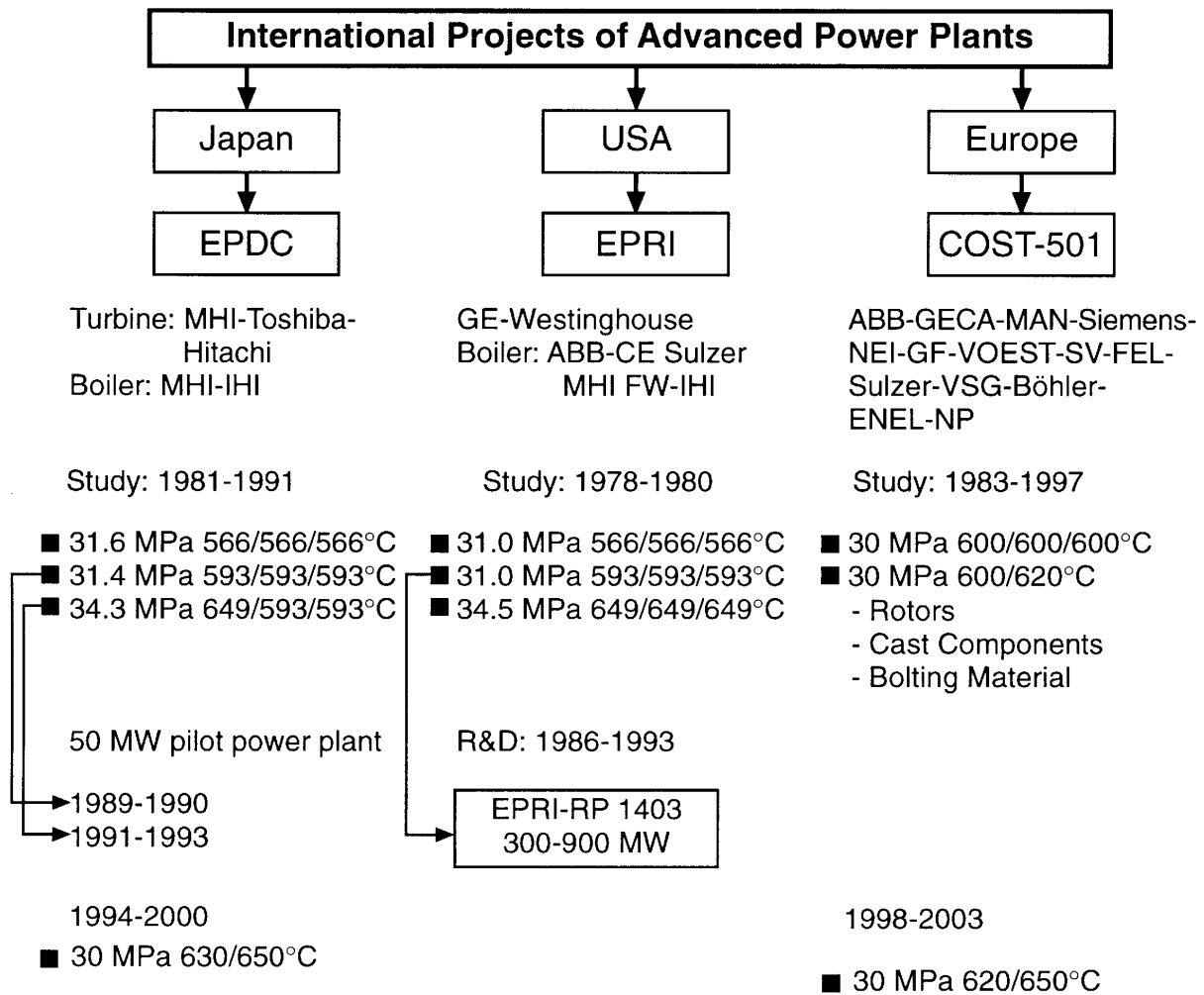


Figure 1-2
International R&D programs for advanced supercritical plant (Ref. 1)

2

BOILER MATERIALS REQUIREMENTS

The key components whose performance is critical for USC plants are high-pressure steam piping and headers, superheater tubing and waterwall tubing. All of them have to meet creep strength requirements. In addition, pipes and headers, being heavy section components, are subject to fatigue induced by thermal stresses. Ferritic/martensitic steels are preferred because of their lower coefficient of thermal expansion and higher thermal conductivity compared to austenitic steels. Many of the early problems in the USC plants were traceable to the use of austenitic steels which were very prone to thermal fatigue. Research during the last decade has, therefore, focused on developing cost-effective, high-strength ferritic steels that could be used in place of austenitic steels. This has resulted in ferritic steels capable of operating at metal temperatures up to 620°C (1150°F), with good weldability and fracture toughness.

Superheater and reheater (SH/RH) tubing application calls for high creep strength, thermal fatigue strength, weldability, resistance to fireside corrosion/erosion and resistance to steamside oxidation and spallation. Thermal fatigue resistance as well as cost considerations would dictate the use of ferritic/martensitic steels. Unfortunately, the strongest of these steels which can be used up to metal temperature of 620°C (1150°F) purely from a creep strength point of view are still limited by fireside corrosion to metal temperature of 593°C (1100°F). This corresponds to a steam temperature of about 565°C since SH/RH metal temperature can exceed the steam temperature by as much as 28°C (50°F). Excessive corrosion of ferritic steels caused by liquid iron-alkali sulfates in the tube deposits is an acute concern in the USA, where high sulfur corrosive coals are used more frequently than elsewhere. Therefore high strength ferritic stainless steels such as T-91 are infrequently used in the U.S. The standard practice is to use T-22 for the lower temperatures and SS304H or SS347 for the highest temperatures.

With respect to waterwall tubing, the concern is twofold. High supercritical pressures and the use of high heat release furnaces will increase the waterwall temperatures to the point that easily weldable low alloy steels such as T-11* (1.25Cr, 0.5Mo) have insufficient creep strength. Higher strength steels such as T-91* are available, but require postweld heat treatments. The second concern is corrosion. Recent results in the USA on boilers retrofitted with low NO_x burner systems, using overfire air, indicate that the present low alloy steels can suffer from excessive corrosion, as high as 2 mm/yr. Weldable high strength alloys clad or overlaid with high Cr alloys have to be utilized to reduce or eliminate excessive corrosion⁽⁷⁾.

All temperatures cited in the paper are steam temperatures unless otherwise specified. For header and piping, metal temperature is nearly equal to the steam temperature. For tubing, the metal temperature is generally higher.

* ASME boiler code steel designation, equivalent pipe steels are designated as P-11, 92, etc., while forgings are designated F-11, 91, etc.

2.1 Historical Evolution of Steels

Masuyama has presented an excellent historical perspective on the development of steels for power plants as shown in Figure 2-1⁽⁸⁾. The figure shows 10^5 h creep rupture strength at 600°C (1112°F) by year of development. They classify the ferritic steel development in terms of 4 generations as follows:

Generation	Years	Alloy Modifications	Strength 10^5 hr Creep Rupture Achieved MPa	Example Alloys	Maximum Metal Use Temp. °C
1	1960-70	Addition of Mo or Nb, V to simple 12Cr and 9Cr Mo steels	60	EM12, HCM9M, HT9, Tempaloy F9, HT91	565
2	1970-85	Optimization of C, Nb, V	100	HCM12, T91, HCM2S	593
3	1985-95	Partial substitution of W for Mo	140	P-92, P-122 (HCM12A, NF616)	620
4	Emerging	Increase of W and addition of Co	180	NF12, SAVE12	650

In the field of austenitic steels, efforts were made from the 1970's to the early 1980's to improve conventional 18Cr-8Ni series steels originally developed as corrosion resistant materials for chemical use, mainly with respect to their creep strength. Another goal pursued from the 1980's to the early 1990's was to improve the creep strength of conventional 20-25Cr series steels having superior oxidation and corrosion resistance.

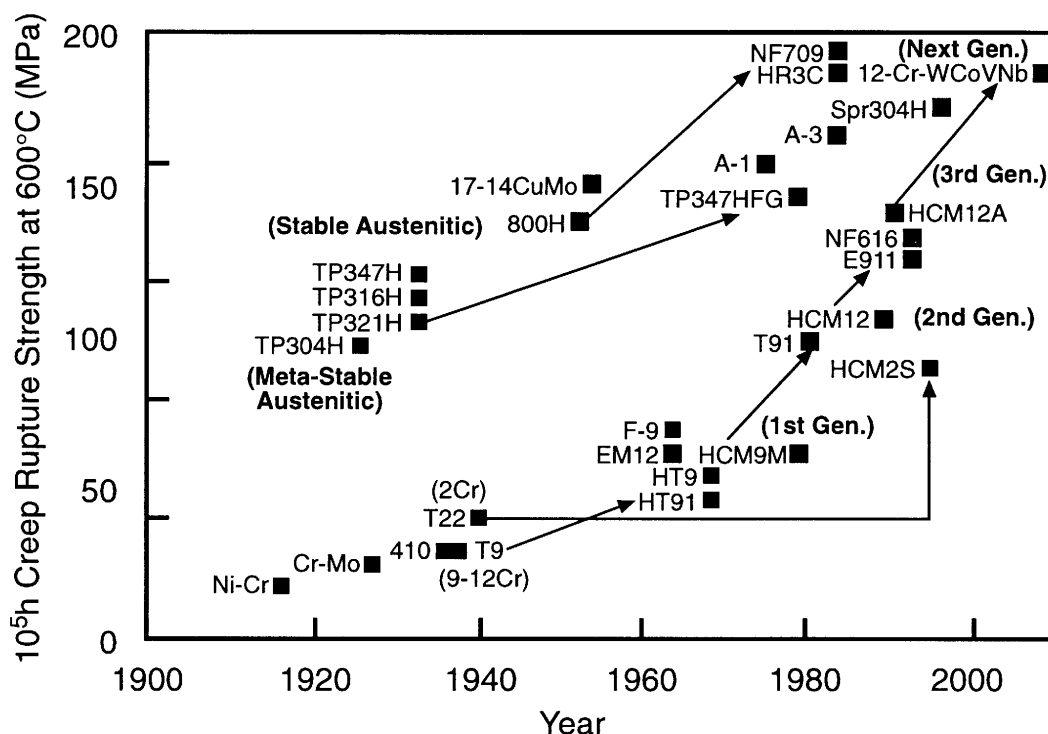


Figure 2-1

Historic evolution of materials in terms of increasing creep rupture strength (8)

2.2 Development Philosophy for Ferritic Steels, Mainly for Use in Thick Section Piping

Table 2-1 shows the chemical compositions of ferritic steels for power boilers. The systematic evolution of these steels has been thoroughly reviewed by Masuyama, as shown in Figure 2-2⁽⁸⁾. Among the 9%Cr steels fully commercialized, the P91 steel has the highest allowable stress and has been extensively used all over the world as a material for headers and steam pipes in ultra supercritical plants operating at steam temperatures up to 593°C (1100°F). Alloy NF616 (P-92), developed by substituting part of the Mo in P91 by W, has an even higher allowable stress and can be operated up to steam temperatures of 620°C (1150°F). E911 is a European alloy similar in composition to NF616 with similar capabilities. Beyond 620°C (1150°F), the 9%Cr steels become limited by oxidation resistance and 12%Cr steel and austenitic steels have to be used.

Among the 12%Cr steels, HT91 has been widely used for tubing, headers and piping in Europe. Use of the steel in Japan and US has been limited due to its poor weldability. HCM12 is an improved version of HT91 with 1% W and 1% Mo, having a duplex structure of δ -ferrite and tempered martensite with improved weldability and creep strength. Further increases in creep strength by substituting more of the Mo with W and addition of Cu has resulted in alloy HCM12A (P-122), which can be used for header and piping up to 620°C (1150°F). Two alloys NF12 and SAVE12 having an even higher creep strength than HCM12A are in the developmental stage. NF12 contains 2.5%Co, 2.6%W and slightly higher B compared to

HCM12A. SAVE12 contains 3% Co, 3% W, and minor amounts of Ta and Nb. These latter elements contribute to strengthening by producing fine and stable nitride precipitates. HCM2S (T-23) a low carbon 2-1/4Cr-1.6W steel with V and Nb is a cost-effective steel with higher creep strength than T22. Because of its excellent weldability without pre- or post-weld heat treatment it is a good candidate for waterwall tubing.

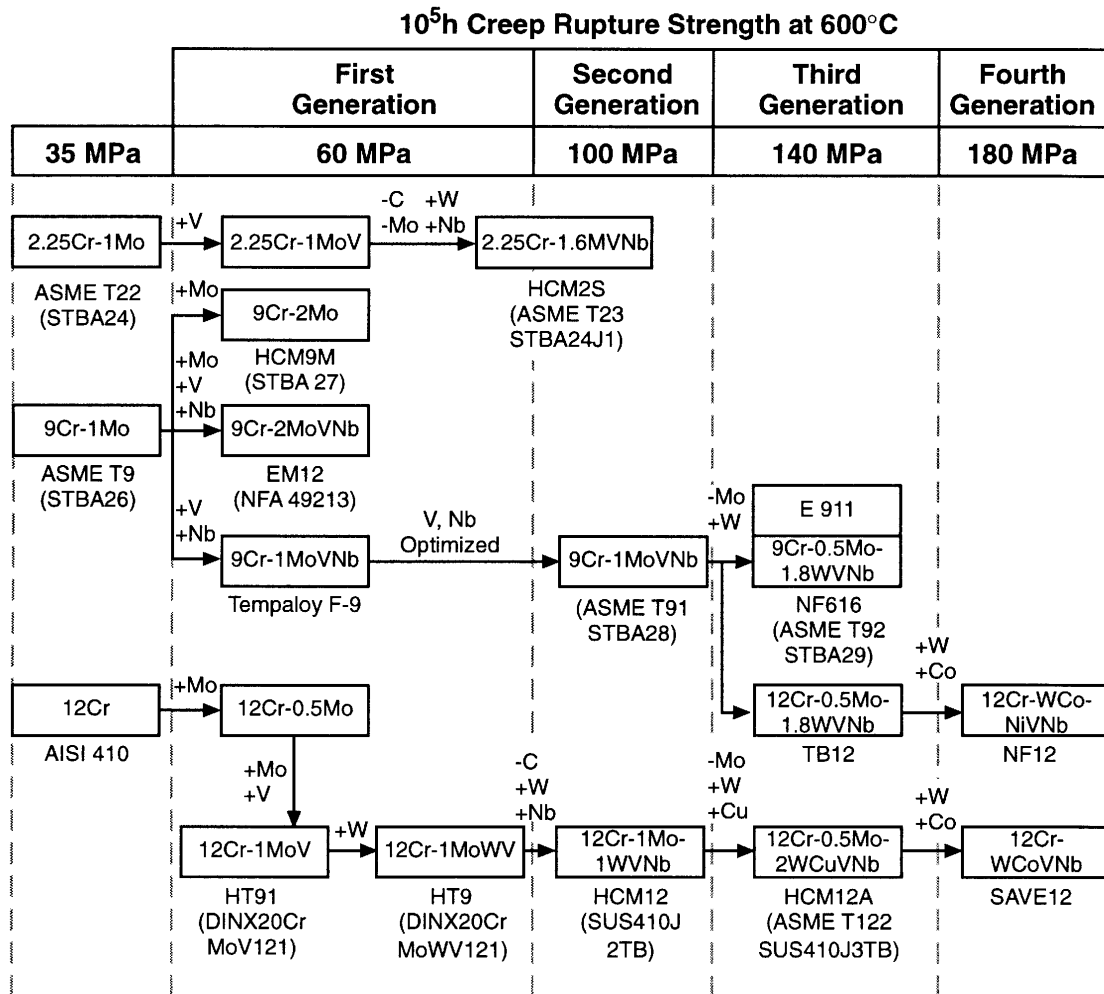


Figure 2-2
Evolution of ferritic steels for boilers (8)

The role of alloying elements in development of the ferritic steels has been extensively investigated. W and Mo and Co are primarily solid solution strengtheners. V and Nb contribute to precipitation strengthening by forming fine and coherent precipitation of M(C, N)X carbonitrides in the ferrite matrix. Vanadium also precipitates as VN during tempering or during creep. The two elements are more effective in combination at levels of about 0.25% V and 0.05% Nb. Chromium contributes to solid solution strength as well as to oxidation and corrosion resistance. Nickel improves the toughness but at the expense of creep strength. Partial replacement of Ni by Cu helps stabilize the creep strength. Carbon is required to form fine carbide precipitates but the amount needs to be optimized for good weldability.

Atom probe results have shown that boron enters the structure of $M_{23}C_6$ and boron segregates to $M_{23}C_6$ - matrix interface (8b). It has also been suggested that boron helps reduce coarsening of $M_{23}C_6$ and that boron also assists in nucleation of VN, the mechanism of “latent creep resistance”^(8b).

Cobalt is an austenite stabilizer and developers of NF12 suggest that is why they used cobalt additions^(8b). Cobalt is known to delay recovery on tempering of martensitic steels. Cobalt also promotes nucleation of finer secondary carbides on tempering. This is attributed both to its effect on recovery and its effect on the activity of carbon^(8b). Cobalt also slows coarsening of alloy carbides in secondary hardening steels. This was suggested to be the result of cobalt increasing the activity of carbon and cobalt not being soluble in alloy carbides^(8b). Results of Hidaka suggest that Co has a positive effect on creep rupture stress in HR1200 type compositions^(8b).

2.3 Development Philosophy for Austenitic Steels, Mainly for Superheater Tubing

Austenitic steels are candidates primarily in the finishing stages of superheater/reheater tubing, where, oxidation resistance and fireside corrosion become important in addition to creep strength. From a creep strength point of view, T91 is limited to 565°C steam (metal 593°C) and NF616, HCM12A and E911 are limited to 593°C steam (metal 620°C). Even the strongest ferritic steel today is limited to 593°C (1150°F) (metal temperature) from an oxidation point of view. At temperatures above these, austenitic steels are required. Hence there has been considerable development with respect to austenitic stainless steels. In actual practice in the U.S. SS304M and SS347 are widely used instead of T-91 in superheater applications, mainly because they are easier to weld, while the cost difference is relatively small.

Table 2-2 lists the compositions of various stainless steels for SH/RH tube applications. The steels fall into four categories: 15Cr, 18Cr, 20-25Cr and higher Cr stainless steels. The various stages in the evolution of these steels have consisted of initially adding Ti and Nb to stabilize the steels from a corrosion point of view, then reducing the Ti and Nb content (understabilizing) to promote creep strength rather than corrosion, followed by Cu additions for increased precipitation strengthening by fine precipitation of a Cu rich phase. Further trends have included austenite stabilization using 0.2% nitrogen and W addition for solid solution strengthening. This development sequence is illustrated in Figure 2-3⁽⁸⁾.

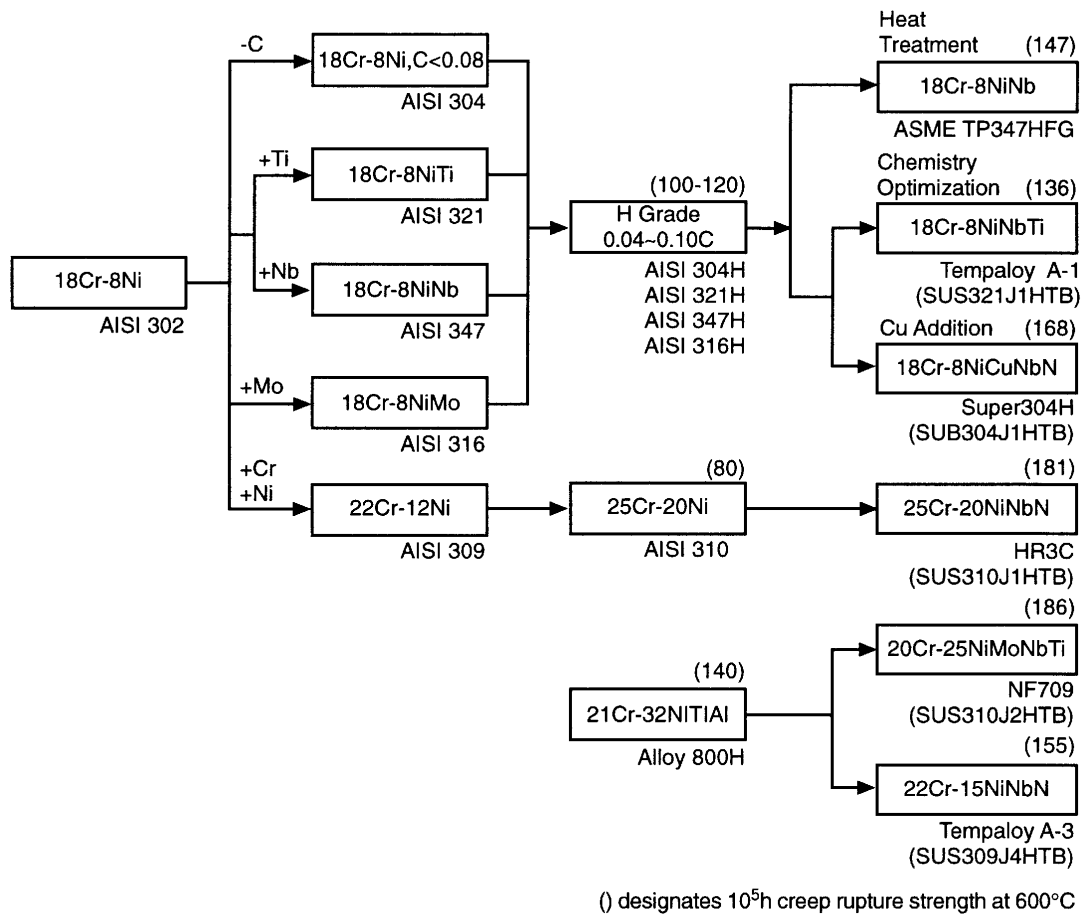


Figure 2-3
Evaluation of authentic steels for boilers (8)

Table 2-1
Nominal Chemical Compositions of Ferritic Steels for Boilers

	Steels	Specification		Chemical Composition (mass%)												Manufacturers
		ASME	JIS	C	Si	Mn	Cr	Mo	W	Co	V	Nb	B	N	Others	
1-1/4Cr	T11	T11		0.15	0.5	0.45	1.25	0.5	--	--	--	--	--	--	--	
	NFIH			0.12	--	--	1.25	1.0	--	--	0.20	0.07	--	--	--	Nippon Steel
2Cr	T22	T22	STBA24	0.12	0.3	0.45	2.25	1.0	--	--	--	--	--	--	--	
	HCM2S	T23	STBA24J1	0.06	0.2	0.45	2.25	0.1	1.6	--	0.25	0.05	0.003	--	--	Sumitomo
	Tempaloy F-2W						2.0	0.6	1.0		0.25	0.05		--	--	NKK
9Cr	T9	T9	STBA26	0.12	0.6	0.45	9.0	1.0	--	--	--	--	--	--	--	Vallourec-Mannesman
	HCM9M	--	STBA27	0.07	0.3	0.45	9.0	2.0	--	--	--	--	--	--	--	Sumitomo
	T91	T91	STBA28	0.10	0.4	0.45	9.0	1.0	--	--	0.20	0.08	--	0.05	0.8Ni	Vallourec-Mannesman Sumitomo
	E911			0.12	0.2	0.51	9.0	0.94	0.9	--	0.20	0.06		0.06	0.25Ni	
12Cr	HT91	(DIN x20CrMoV121)		0.20	0.4	0.60	12.0	1.0	--	--	0.25	--	--	--	0.5Ni	Vallourec Mannesman
	HT9	(DIN x20CrMoWV121)		0.20	0.4	0.60	12.0	1.0	0.5	--	0.25	--	--	--	0.5Ni	Vallourec Mannesman
	Tempaloy F12M						12.0	0.7	0.7	--						NKK
	HCM12		SUS410J2TB	0.10	0.3	0.55	12.0	1.0	1.0	--	0.25	0.05		0.03	--	
	TB12	--	--	0.08	0.05	0.50	12.0	0.50	1.8	--	0.20	0.05	0.30	0.05	0.1Ni	
	HCM12A	T122	SUS410J3TB	0.11	0.1	0.60	12.0	0.4	2.0	--	0.20	0.05	0.003	0.06	1.0Cu	Sumitomo
	NF12	--	--	0.08	0.2	0.50	11.0	0.2	2.6	2.5	0.20	0.07	0.004	0.05	--	Nippon Steel
	SAVE12	--	--	0.10	0.3	0.20	11.0	--	3.0	3.0	0.20	0.07	--	0.04	0.07Ta, 0.04Nd	Sumitomo

Boiler Materials Requirements

Table 2-2
Nominal Chemical Compositions of Austenitic Steels for Boiler (wt%)

	Specifications													
	ASME	JIS	C	Si	Mn	Ni	Cr	Mo	W	V	Nb	Ti	B	Others
18Cr-8Ni	TP304H	SUS304HTB	0.08	0.6	1.6	8.0	18.0	--	--	--	--	--	--	--
	Super 304H	SUS304J1HTB	0.10	0.2	0.8	9.0	18.0	--	--	--	0.40	--	--	3.0Cu, 0.10N
	TP321H	SUS321HTB	0.08	0.6	1.6	10.0	18.0	--	--	--	--	0.5	--	--
	Tempaloy A-1	SUS321J1HTB	0.12	0.6	1.6	10.0	18.0	--	--	--	0.10	0.08	--	--
	TP316H	SUS316HTB	0.08	0.6	1.6	12.0	16.0	2.5	--	--	--	--	--	--
	TP347H	SUSTP347HTB	0.08	0.6	1.6	10.0	18.0	--	--	--	0.8	--	--	--
	TP347 HFG		0.08	0.6	1.6	10.0	18.0	--	--	--	0.8	--	--	--
15Cr-15Ni	17-14CuMo		0.12	0.5	0.7	14.0	16.0	2.0	--	--	0.4	0.3	0.006	3.0Cu
	Esshete 1250		0.12	0.5	6.0	10.0	15.0	1.0	0.2	1.0	--	0.06	--	
	Tempaloy A-2		0.12	0.6	1.6	14.0	18.0	1.6	--	--	0.24	0.10	--	
20-25Cr	TP310	SUS310TB	0.08	0.6	1.6	20.0	25.0	--	--	--	--	--	--	
	TP310NbN	SUS310J1TB	0.06	0.4	1.2	20.0	25.0	--	--	--	0.45	--	--	0.2N
	NF707*		0.08	0.5	1.0	35.0	21.0	1.5	--	--	0.2	0.1	--	--
	Alloy 800H	NCF800HTB	0.08	0.5	1.2	32.0	21.0	--	--	--	--	0.5	--	0.4Al
	Tempaloy A-3*	SUS309J4HTB	0.05	0.4	1.5	15.0	22.0	--	--	--	0.7	--	0.002	0.15N
	NF709*	SUS310J2TB	0.15	0.5	1.0	25.0	20.0	1.5	--	--	0.2	0.1	--	
	SAVE25*		0.10	0.1	1.0	18.0	23.0	--	1.5	--	0.45	--	--	3.0Cu, 0.2N
HighCr-HighNi	CR30A*		0.06	0.3	0.2	50.0	30.0	2.0	--	--	--	0.2	--	0.03Zr
	HR6W*		0.08	0.4	1.2	43.0	23.0	--	6.0	--	0.18	0.08	0.003	
	Inconel 617			0.40	0.4	54.0	22.0	8.5	--	--	--	--	--	12.5Co, 1.2Al
	Inconel 671**		0.05	--	--	51.5	48.0	--	--	--	--	--	--	--

* Not ASME code approved.

** Low strength material for use in co-extruded tubing. For weld overlays, IN72 (44%Cr-bal Ni) is the matching weld wire.

2.4 Choice of Materials for Headers and Steam Pipes

Material-property requirements for headers and steam pipes are likely to be similar, and hence they have been grouped together in the following discussion. Some minor differences exist which may affect material selection. The steam temperature is likely to be much more uniform in steam pipes, but subject to time-dependent and location-dependent fluctuations in headers. Hence, the thermal-fatigue-strength requirements are greater for headers than for steam pipes. Self-weight-induced stresses are less important for headers than for steam pipes, permitting heavier-wall construction and an attendant higher temperature/pressure capability for a given material when used in headers. One of the most important differences is that headers have many welded attachments to inlet stub tubes from reheaters and superheaters and intersections of outlet nozzles connecting pipework. Depending on the selection of materials for the superheater/reheater tubes and the header piping, dissimilar-metal welded joints may be required. The integrity of such austenitic-to-ferritic welds when 9 to 12%Cr steels form the ferritic components needs to be more thoroughly investigated.

Headers and pipes have traditionally been made from low alloy steels such as P11 and P22 in the USA. Even in conventional boilers, such headers can fail due to thermal fatigue cracking, caused by cycling. A common failure mode is the cracking of the ligaments between the tube boreholes⁽⁹⁾. The use of higher temperatures and pressures can only increase the problem. Previous attempts to use austenitic steels have not been successful due to high thermal expansion of these steels.

Several candidate ferritic steels have emerged succeeding the P11 and P22 steels, which are capable of operation up to 593°C (1100°F). These include HT9, HT91, HCM9M, HCM12 and P91.

Alloys HT9 and HT91 are well-established steels with an extensive stress-rupture database which exceeds 10^5 h at temperatures in the range 500 to 600°C (930 to 1110°F) for all product forms. There is also extensive operating experience (>20 years) in Germany, Belgium, Holland, south Africa, and Scandinavia for steam temperatures up to 540°C (1000°F) and some limited experience on a few small units with steam temperatures from 560 to 580°C (1040 to 1075°F). This experience generally has been satisfactory. Difficulties have, however, been reported during fabrication and particularly during welding and post-weld heat treatment. This arises because the relatively high carbon content of the steel (0.2%) and the correspondingly low M_s temperature promote the possibility of austenite retention after welding, high residual stresses, and cracking prior to and during stress relief. It is reported that these problems have been overcome by careful control of preheat treatment and postweld heat treatment backed up by vigorous quality control. Difficulties have also been reported when the material has been given inadequate solution heat treatment. Due to these concerns, these alloys have not found much favor in the United States, the United Kingdom, or Japan. Alloys with improved weldability characteristics, such as HCM12M have been adequately characterized for tubing and large-diameter, thick-wall pipes.

With regard to the 9Cr-2Mo steel (HCM9M), the feasibility of fabrication of large-diameter, thick-wall piping and application to in-plant header and main steam piping was first

demonstrated in 1985⁽¹⁰⁾. The practical use of this material has been easy because its simple composition lends fabricability and weldability comparable to those of low-alloy steels. The toughness of large-diameter pipes has been found to be over 102 J/cm² (460 ft-lb/in.²) at 0°C (32°F). Allowable stresses are comparable to those for the HT9 alloy, but lower than those for P91. Service experience of nearly 25 years have been accumulated since the alloy was developed with about 2000 tons having been produced specifically for SH/RH tubes and steam pipes.

The modified 9Cr alloy, P91, appears to be quite superior to HT9, HT-91 and to HCM9M in terms of creep-rupture strength and is, hence, the most promising candidate for use in header and steam piping for temperatures up to 595°C (1100°F). One of the early applications was by the Chubu Electric Power Company (Kawagoe Power Station, Units 1 and 2) for 565°C (1050°F) steam conditions as headers and steam pipes. A majority of the European supercritical plants listed in Table 1-2 have utilized P91 as main steam and reheat piping⁽⁶⁾. Numerous retrofit applications have also been carried out for headers/steam pipes⁽⁶⁾. The alloy was approved by the ASME Boiler Code Committee for various uses between 1983 and 1986 as T, P, F-91*. Since that time, the alloy has found applications worldwide and is available from many sources, since the composition is not proprietary. It is especially popular in Europe, where it proved superior in creep strength as well as weldability, compared to the well-known HT91 steel, used in supercritical boilers.

The high creep strength of grade 91 steel is due to small additions of V, Nb and nitrogen, which lead to the precipitation of M₂₃C₆ carbides and (Nb, V) carbonitrides, in addition to solution strengthening by Mo. Very extensive studies were made world wide to evaluate the suitability of P-91 for heavy section components. These included manufacturing studies, welding trials, both similar and dissimilar, bending trials, both hot and cold, and various mechanical tests, on both virgin and aged samples^(11,12). The net result of all these tests is that P-91 is now the preferred heavy section materials for supercritical boilers worldwide. However, most designers feel the use of P-91 will probably be limited to steam conditions of about 593°C/25 MPa. This is especially the case in Europe, where the allowable creep strength is about 10% lower than in Japan and the U.S.

Fortunately, Professor Fujita in Japan discovered that the creep strength of 9-12Cr, Mo, V, Nb steels can be raised by about 30% through partial substitution of Mo by W⁽¹³⁾. This has spawned another round of intensive alloy development and evaluation worldwide⁽¹⁴⁾. Two of these steels, a 9Cr steel developed by Nippon Steel NF616 (P-92) and a 12Cr steel HCM12A developed by Sumitomo metals (P-122) have been approved for use in boiler heavy section components by ASME. Another W containing steel E-911 is in advanced development in Europe. The allowable strength of the new steels at 600°C is about 25% higher than that of P-91. Thus these steels should allow steam temperatures up to 620°C and pressures up to 34 MPa.

Figure 2-4 shows a plot of the allowable stress at various temperatures for ferritic steels⁽⁸⁾. The figure clearly shows the enormous advances in the materials technology which have been made in the last 20 years. Especially at the higher temperatures, the most advanced steels show allowable stresses that are nearly 2.5 to 3 times that of the workhorse steel in conventional

* T = tubing, P = pipe, F = forging

plants, i.e., 2-1/4Cr-1Mo steel (P22). The layering of the alloys into the different generations described earlier is also evident. HCM12A (P122), NF616 (P92) and E911 emerge as the three highest strength alloys suitable for ultra supercritical plants up to 620°C, followed by T91, HCM12, EM12, HCM9M and HT91 suitable for intermediate temperatures up to 593°C followed by T22 for use up to 565°C (1050°F). NF12 and SAVE12 are still developmental but are expected to meet the Phase 2 goals. This rationale has been incorporated in the materials selection shown in Table 2-3.

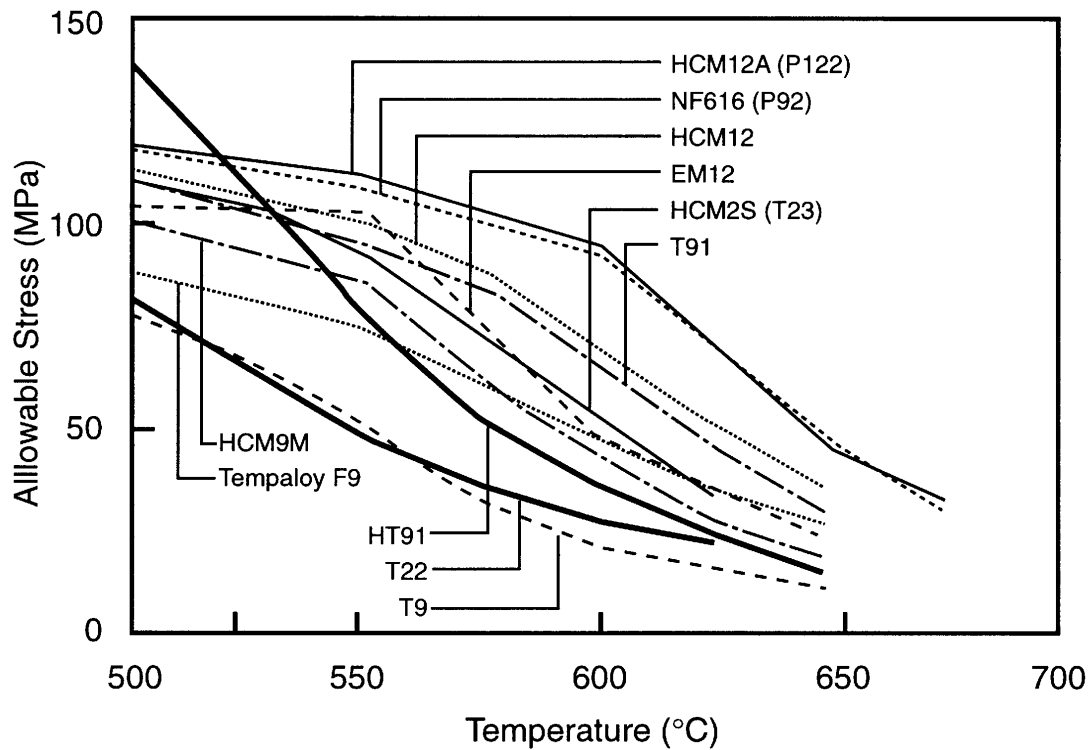


Figure 2-4
Comparison of allowable stresses of ferritic steels for boiler (8)

Table 2-3
Candidate Materials for Advanced Supercritical Plants for Various Steam Conditions

Component	Phase 0 31MPa (4500 psi) 565/565/565°C (1050/1050/1050°F)	Phase 1 31MPa (4500 psi) 593/593/593°C (1100/1100/1100°F)	Phase 1B 31MPa (4500 psi) 620/620/620°C (1150/1150/1150°F)	Phase 2 34.5MPa (5000 psi) 650/650/650°C (1200/1200/1200°F)
Headers/steam pipes	P22, HCM2S (P23) P91, P92, P122	P91, P92, P122, E911	P92, P122 E911, NF12, SAVE12	SAVE12 ⁺ NF12 ⁺
Finishing SH non-corrosive	T91, 304H, 347	TP347 HFG Super 304 H/P-122*	NF 709 Super 304 H	NF 709 Inconel 617
Corrosive	310 NbN (HR3C)	310 NbN (HR3C) SS347/IN72**	310 NbN (HR3C) Super 304H/IN72**	Cr 30A NF 709/IN72**
Finishing RH	Same as SH	Same as SH	Same as SH	Same as SH
Water wall				
Lower wall	C steel	T11, T12, T22	Same as Phase 1	
Upper wall	T11, T12, T22	T23 (HCM12)	Same as Phase 1	
For low NO _x Boilers + High S coal	Clad with alloy containing >20% Cr or chromized	Same as Phase 0	Same as Phase 0	Same as Phase 0

* High strength ferritic alloys with 9%Cr are suitable for steam piping and headers, but may suffer excessive fire side oxidation. 12Cr steels may be suitable, but further testing is needed.

** IN72 (44Cr, bal Ni) weld overlay for corrosion protection

⁺ Developmental Alloy

A very interesting fact is that application of the new steels may actually result in a capital cost reduction. Figure 2-5 shows the allowable design stresses and a comparison of the relative wall thicknesses at various temperatures⁽¹⁵⁾. At any given temperature, higher allowable stresses for a material permits design of thinner wall headers/pipes. This not only reduces thermal stresses, but also reduces cost. From Figure 2-5, section thicknesses and materials costs can be calculated as a function of temperature and pressure. Figure 2-6 shows the results for a pressure of 31 MPa (4500 psi). The cost of using high strength steel becomes lower than that of P-22 steel at about 520°C. The cost of using the W containing steel is lower than that of P-91 above about 550°C. These relations do not change very much with decreasing pressure down to 20 MPa (3000 psi). Actual fabricated and installed cost differences should be even larger as the thinner pipes need less welding and are easier to install. Fewer supports are needed thus reducing costs further.

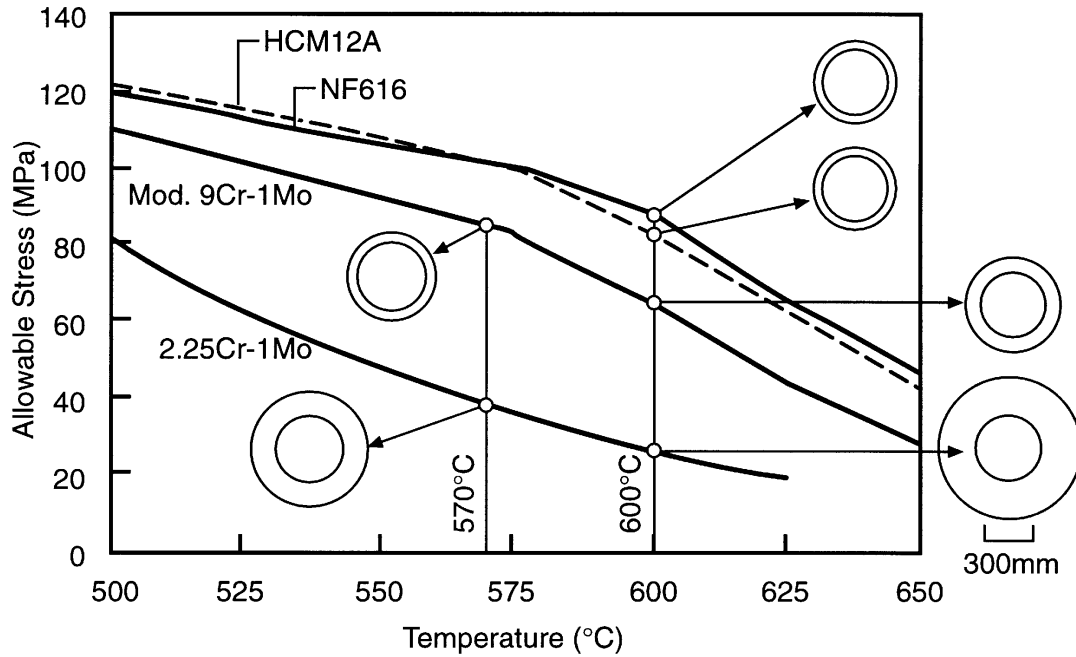


Figure 2-5
Comparison of allowable stresses and sectional view of main steam pipes designed at 570°C and 600°C (15)

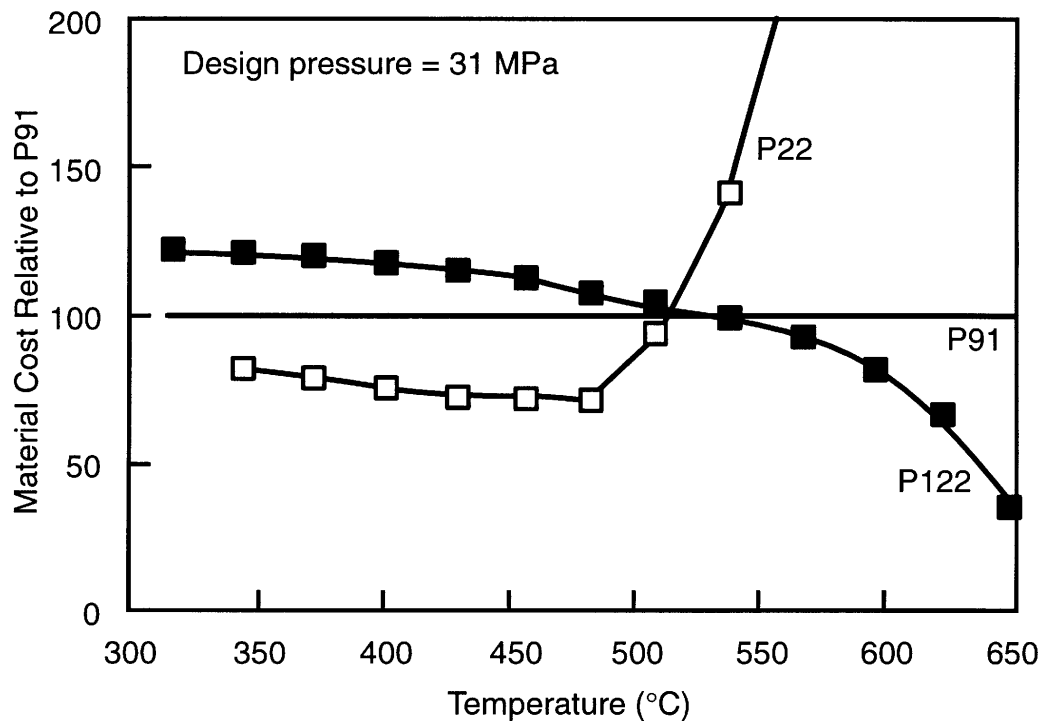


Figure 2-6
Cost of P-22, P-91 and P-122 steels header materials as a function of temperature at 31 Mpa steam pressure (15)

Boiler Materials Requirements

A sample list of European installations using the most advanced steels NF616 (P92), HCM12A (P122) and E911 is shown in Table 2-4⁽⁶⁾. There is considerable interest in using these alloys for outlet headers and main steam and reheat pipe work. Full-scale headers have been being installed in a 415MW supercritical plant under consideration by the Danish utility, ELSAM. Headers using P92 and P122 have been constructed and installed. Two of the headers will be tested under accelerated high-temperature conditions in a high-pressure cell operated by Mitsubishi Heavy Industries.

Table 2-4
Application of New Tungsten-Bearing Steels in European Power Stations (Ref. 6)

Power Station	Material Grade	Size	Component	Steam Conditions°C/MPa	Installation
Vestkraft Unit 3	P92 (NF616)	ID 240 x 39	Straight Pipe Main Steam	560/25	1992
Nordjyllands-vaerket	P92 (NF616) P122 (HCM12A)	ID 160 x 45	Header	582/29	1996
Schkopau Unit B	E911	ID 550 x 24	Induct. Bend Hot Reheat	560/7	1996
Staudinger Unit 1	E911	ID 201 x 22	Induct. Bend Main Steam	540/21.3	1996
Skaerbaek Unit 3	E911	ID 230 x 60	Induct. Bend Main Steam	582/29	1996
GK Kiel	P92	ID 480 x 28	Header	545/5.3	1997
VEW	E911	OD 31.8 x 4	Superheater	650	1998
Westfalen	E911	ID 159 x 27	Steam Loop	650/18	1998
Westfalen	P92	ID 159 x 27	Steam Loop	650/18	1998

Some additional design considerations in applying the advanced ferritic steels are as follows:

1. The high temperature strength of the advanced alloys (e.g., P-92, P-122, E911) is essentially the same as that of austenitic alloys. But oxidation resistance is less than that of austenitic alloys. This parameter of advanced 9 to 12Cr alloys must be more fully evaluated prior to application to high temperature parts.
2. Post weld heat treatment (PWHT) is always required for welded joints of advanced 9 to 12 Cr alloys to ensure minimal stress and optimal ductility. Design must be made to reduce field heat treatment as much as possible to keep production and PWHT costs minimal.
3. In the weldment of dissimilar alloys, material selection must be based on consideration of PWHT temperature. For example, the 9Cr-1Mo alloy and 1Cr-0.5Mo steel would not be acceptable materials for the case of joints in a longitudinal direction; measures must be taken to consider the behavior of welded joint creep rupture strength.
4. Last but not least, is the apparent susceptibility of ferritic steel welds to Type IV cracking, which occurs at the edges of fine grained HAZ material adjacent to unaffected parent material. Susceptibility to this has been clearly demonstrated for 1/2CrMoV, 2-1/4Cr-1Mo and 9Cr-1Mo (T91) steels. Safety margins of 10 to 20% are sometimes adopted to provide

for this mechanism. Since the problem in girth welds is primarily associated with bending stresses, the problem can be overcome by proper plant design and maintenance. This issue has therefore been generally glossed over.

2.5 Choice of Materials for Superheater/Reheater Tubes

The superheater tubes in the boiler are likely to undergo the most severe service conditions and must meet stringent requirements with respect to fire-side corrosion, steamside oxidation, creep rupture strength and fabricability. In addition, they must be cost-effective.

2.5.1 Creep Rupture Strength

In terms of creep rupture strength, application of ferritic steels for tubes follow the same logic as for the headers/pipes discussed earlier. Thus, tubes made of T22 should be limited to steam temperature of 538°C (1000°F); Alloys T91, HCM12, EM12, HCM9M and HT91 limited to steam temperature of 565°C (1050°F); Alloys T-92, P-122 and E911 limited to steam temperature of 593°C (1100°F). Under corrosive conditions however, even the best ferritic steel may be limited to 563°C (1050°F) temperature and austenitic steels are needed. Although the creep resistance of 12Cr steels is adequate for use at 593°C, there is considerable doubt about their fireside oxidation resistance, especially that of 9Cr steels. Thus 12Cr steels, such as P122 are preferred.

In practice, the high Cr, high strength ferritics have found little use in the U.S. because of perceived welding problems (T-23 may change this). T-22, SS304H and SS347 are the steels most commonly used in supercritical boilers (3500 psi) in the USA.

For convenience, austenitic steels can be classified as those containing less than 20% Cr and those containing more than 20% Cr. Alloy modifications based on the 18Cr-8Ni steels, such as TP304H, 316H, 347H, and Tempaloy A-1, and alloys with lower chromium and higher nickel contents, such as 17-14 CuMo steel, Esshete 1250, and Tempaloy A2, fall into the classification of steels with less than 20% Cr. The allowable tensile stresses for steels in this class are compared in Figure 2-7. Tempaloy A1, Esshete 1250, and 17-14 CuMo steel are found to offer major improvements over the 300 series stainless steels. It has been reported that grain-size modifications of AISI type 347H stainless steel can in some instances lead to rupture properties somewhat better than those of Tempaloy A-1⁽¹⁶⁾.

Several high-creep-strength alloys containing more than 20% Cr, such as NF707, NF709, and HR3C, have been developed, and offer low-cost alternatives to Incoloy 800 for use in the temperature range from 650 to 700°C (1200 to 1290°F). A comparison of the ASME Code allowable stresses for the high-chromium alloys is shown in Figure 2-8. Clearly, NF709 and HR3C are leading candidates for use in the highest-temperature applications. The latter steel was approved for use in boilers by ASME as SS310NbN. The highest creep strength is achieved in Inconel 617, which contains 22% Cr, but it is also likely to be the most expensive alloy to use, due to its high Ni content.

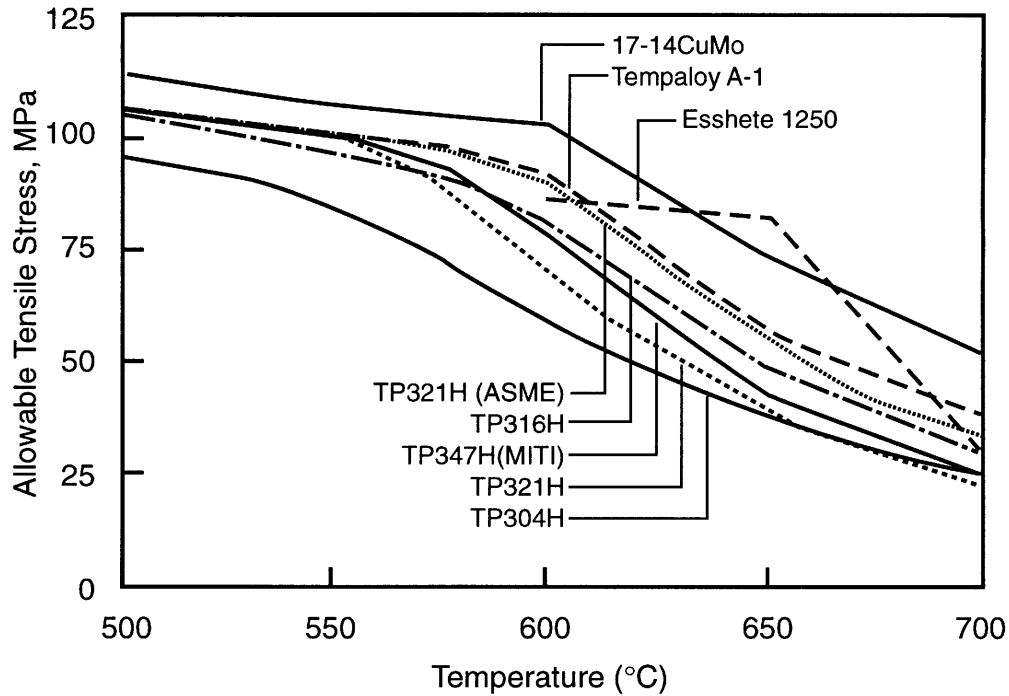


Figure 2-7
Comparison of allowable stresses for 18Cr-8Ni and 15Cr steels (Ref. 17)

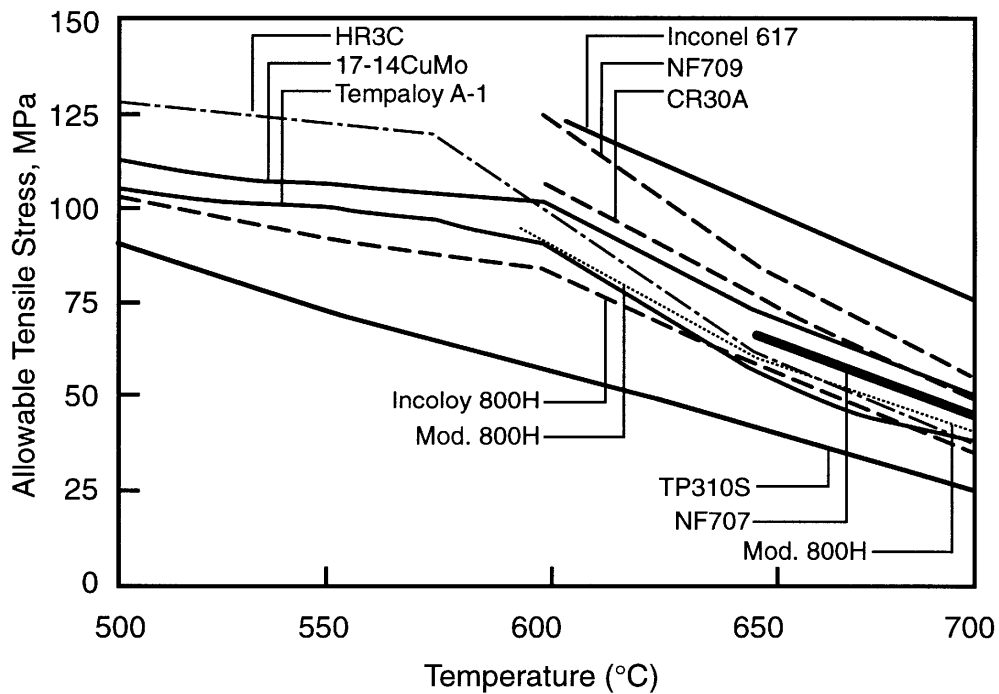


Figure 2-8
Comparison of allowable stresses for austenitic alloys containing more than 20% Cr (based on Ref. 17)

A comparison of allowable temperatures at a constant allowable stress of 49 MPa (7 ksi), as a function of chromium content, is shown in Figure 2-9. With increasing chromium, a discontinuity is seen in the allowable metal temperatures of austenitic steels, rising about 50°C (90°F) above those of ferritic steels⁽¹⁷⁾. In terms of increasing temperature capability, stable austenitic alloys offer the highest capability, followed by metastable austenitic steels, and then by ferritic steels. The fully enhanced, stable austenitic alloys are clearly capable of operating under phase 2 steam conditions (650°C, or 1200°F).

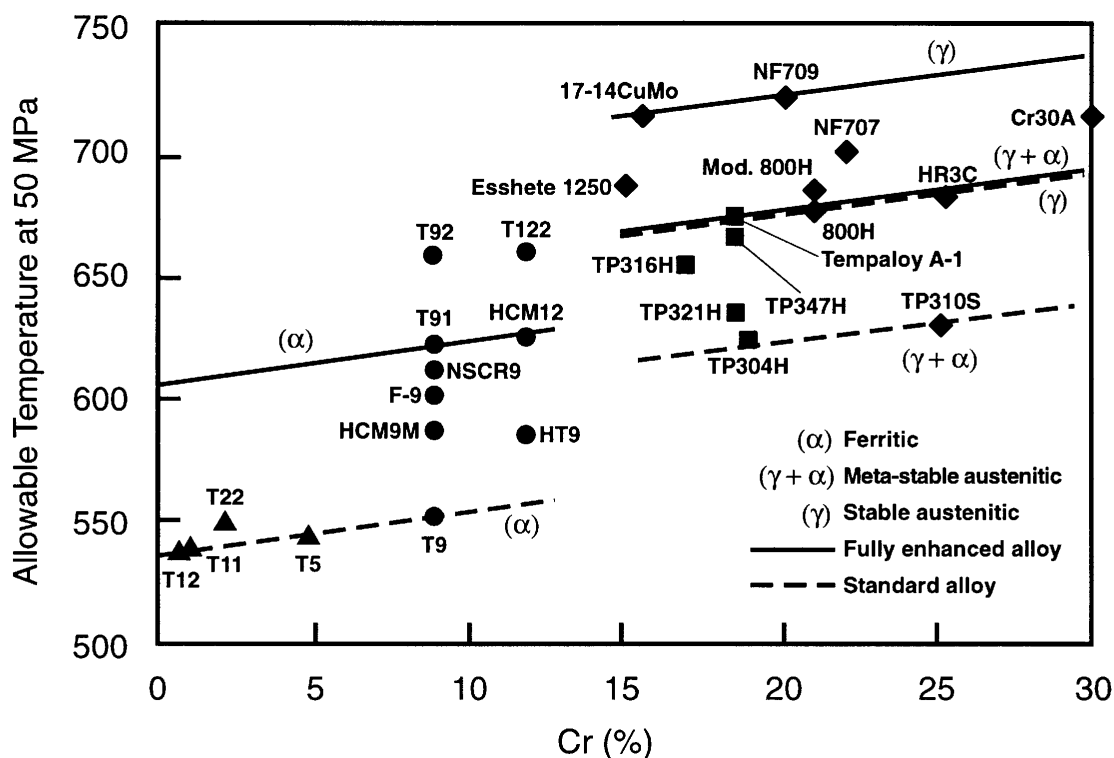


Figure 2-9

Allowable metal temperatures at constant allowable stress of 49 Mpa (7 ksi) as a function of chromium content for various alloys (Ref. 17)

2.5.2 Fire-side Corrosion

Fireside corrosion results from the presence of molten sodium-potassium-iron trisulfates. Because resistance to fire-side corrosion increases with chromium content, the 9 to 12% Cr ferritic steels are more resistant than the 2-1/4Cr-1Mo steels currently used. The 12% Cr steel in turn shows better corrosion resistance than 2-1/4% Cr steel and 9% Cr steel, as shown in Figure 2-10 (18). Stainless steels and other superalloys containing up to 30% Cr represent a further improvement. Increasing the chromium content beyond 30% results in a saturation effect on the corrosion resistance at least in the laboratory, as shown in Figure 2-11(19). For practical purposes, when corrosive conditions are present, fine distinctions between ferritic steels may be academic, and it is usually necessary to use austenitic steels containing chromium in excess of 20%.

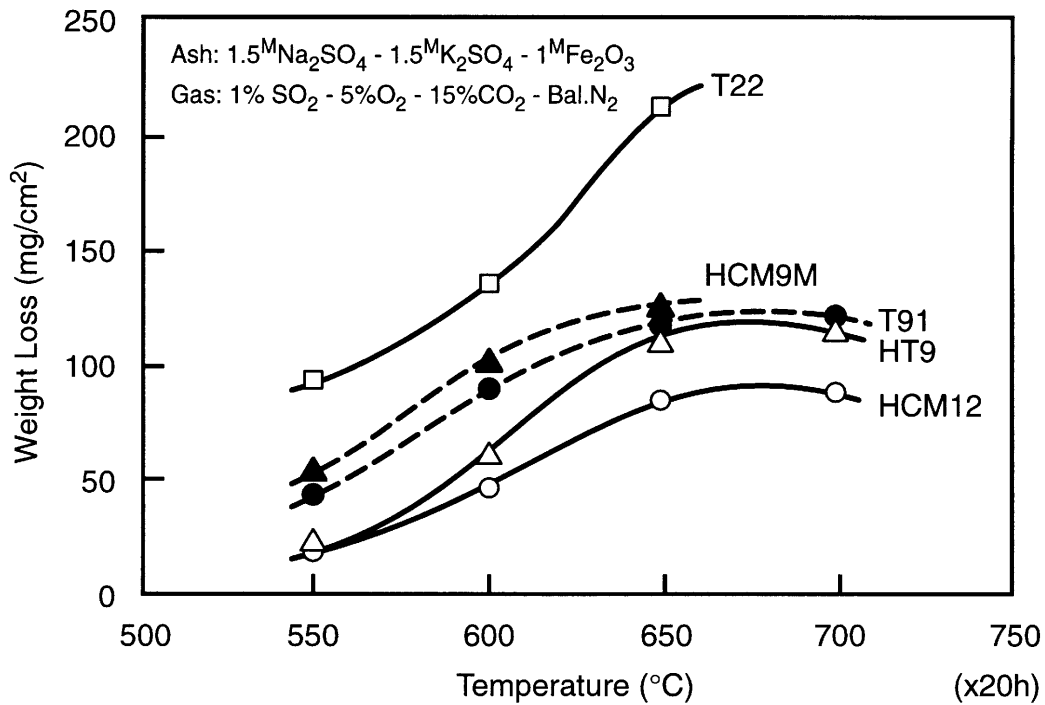


Figure 2-10
 Relationship between hot-corrosion weight loss and temperature for ferritic steels (18)

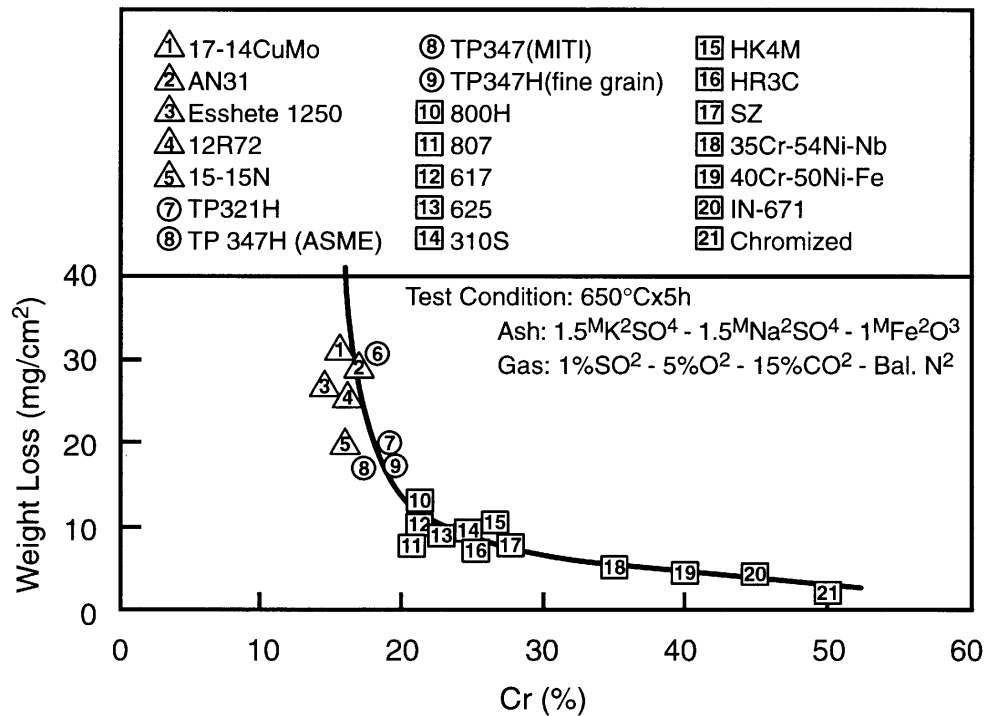


Figure 2-11
 Relationship between hot-corrosion weight loss and chromium content for various alloys (19)

A ranking of the performance of various austenitic alloys in the presence of trisulfates has been provided by Ohtomo *et al.*⁽²⁰⁾ on the basis of short-term laboratory tests (see Fig. 2-12). The plots of weight loss versus temperature exhibit a bell-shape curve. At temperatures below 600°C (1110°F), corrosion is believed to be low because the trisulfate exists in solid form. Above 750°C (1380°F), corrosion rates are once again low, as the trisulfates vaporize. The worst corrosion problem is in the range 600 to 750°C (1110 to 1380°F). The data indicate that the high-chromium alloys such as type 310 stainless steel and Incoloy 800H are superior to the other alloys tests, and that Inconel 671 (Ni-50Cr) or its matching weld metal IN72 is virtually immune to attack. Lower-chromium stainless steels, such as type 316H, type 321H, and Esshete 1250, show considerable susceptibility to attack. The alloy most susceptible to attack seems to be the 17-14 CuMo alloy used in the Eddystone 1 plant. Results of field probe studies confirm the following ranking of alloys in increasing order of corrosion resistance: T91, HCM12, type 347 stainless steel, Incoloy 800, and Inconel 671⁽²¹⁾. In addition to alloy selection, other “fixes” to minimize fire-side corrosion, such as shielding of the tubes may also be applied, if economical⁽²²⁾.

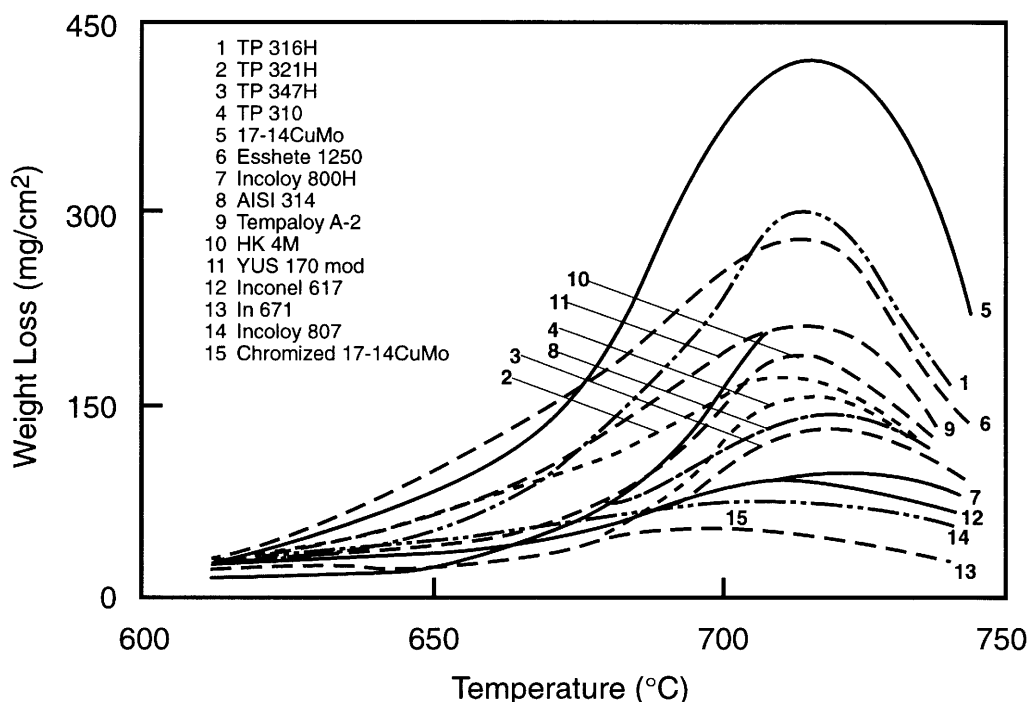


Figure 2-12
Comparison of fire-side corrosion resistance of various alloys (20)

Results of extensive field tests have also been reported by Blough⁽²³⁾. This was based on a collaborative study by EPRI, IHI and F-W who carried out extensive laboratory and field tests in 3 boilers, two of them fueled with somewhat corrosive Eastern bituminous US coal, one fueled with a supposedly non-corrosive Western low sulfur subbituminous coal. The experiments were carried out using air cooled, retractable probes, inserted in finishing superheater or reheater areas. Metal temperatures were maintained in the 600-690°C range (1250-1300°F). Exposure time was 16,000 hrs with samples removed after 4000, 12,000 and 16,000 hrs. Figure 2-13 shows metal losses observed in one of the boilers, using an Eastern bituminous coal, Figure 2-14 those observed in the boiler using subbituminous Western coal. The losses observed were about

the same but the corrosion mechanisms were different. Tubes from the boilers using eastern bituminous coals showed the classic liquid ash corrosion in the 10 and 2 o'clock positions of the tube, where sulfur rich fly ash impacts on the tube. Potassium rich sulfate was found in the ash deposits, and metal wastage was caused by internal oxidation and sulfidation, because a fully protective Cr_2O_3 scale could not form in the presence of sulfur rich deposits. With increasing Cr content in the alloy the Cr_2O_3 scale became more protective, but in all alloys internal oxidation and sulfidation occurred in Cr depleted zones below the scale.

The corrosion morphology of the tubes from the boiler using Western subbituminous coal was similar, but the area of major attack was on the side of the tube facing away from the flue gas stream, where deposits rich in very fine CaSO_4 were found.

From the results presented above, it may be concluded that substantial superheater corrosion can occur, especially in high strength austenitic alloys with a low chromium content. For most coals, high strength modified Alloy 800 type alloys such as NF709, will probably have sufficient corrosion resistance, while for more corrosive coals modified SS 310 type alloys, e.g. HR3C, should given an extra margin of safety. It is of interest to note here that the T-91 sample exposed in the low sulfur coal fueled boiler had a corrosion loss similar to SS 347, which is considerably less than that of SS 304 and 17-14CuMo. A probable reason is that scales and deposits usually adhere tight to ferritic/martensitic steels, but spall readily from all austenitic steels.

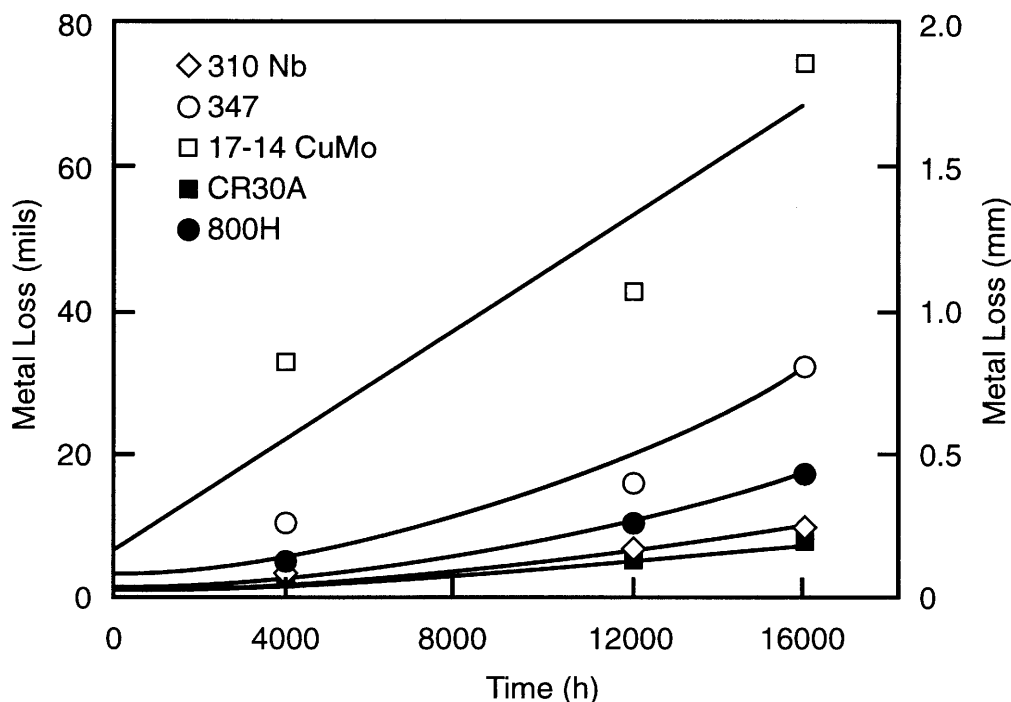


Figure 2-13
Metal losses of various superheater steels in a boiler using bituminous eastern U.S. coals
(23)

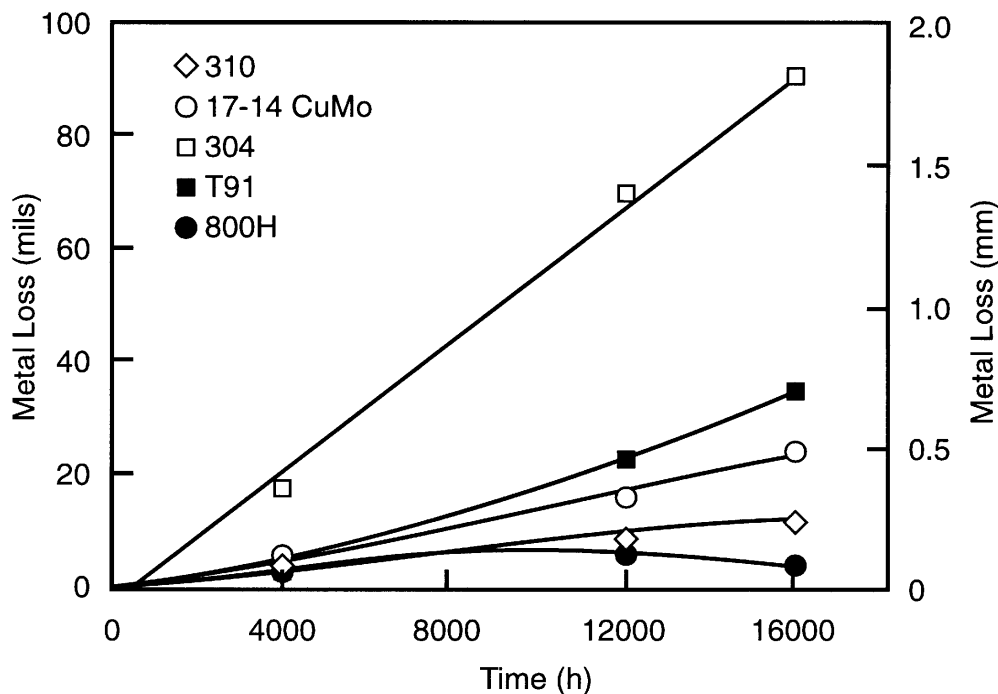


Figure 2-14
Metal losses of various superheater steels in a boiler subbituminous western U.S. coals
(23)

Based on the favorable results from the air-cooled probes in one of the plants, the SS304M reheater, which suffered from severe alkali sulfate corrosion was replaced by one made from SS310 NbN (HR3C).^(23a) Test sections of other alloys were built into the reheater and carefully monitored. It was found that 310NbN (HR3C) was a satisfactory material for 90% of the reheater, with less than 0.25 mm/yr (10 mils/yr) corrosion. However in one area, about 10 tubes wide and 10 ft (3m) high, corrosion rates ranged from 0.5 – 1.25 mm/yr (20-50 mils/yr). Here the corrosion resistance of SS310 was about the same as that of SS347 and alloy 800H. Only a Cr-Ni steel (Cr30A) with 30% Cr had significantly lower corrosion rates, ranging from 0.125 – 0.5 mm/yr (5 – 20 mils/yr). It is concluded that increasing the Cr content of the alloy from 18-20% to 23-25% will only significantly increase corrosion resistance, when the corrosivity of the deposits is moderate, i.e. ≤ 0.5 mm/yr (20 mils/yr for 18-8 stainless steels). For more corrosive conditions, co-extruded tubes or weld overlay claddings containing at least 40% Cr are strongly recommended.

2.5.3 Steam-side Oxidation

Steam-side oxidation of tubes and exfoliation of the oxide scale and its consequence in terms of solid-particle erosion damage to the turbine are well known. This problem is expected to be more severe in advanced steam plants, because the much higher steam temperatures employed are likely to cause more rapid formation of oxide scale.

Very limited data are available regarding the steam-side scale-growth characteristics of the ferritic tubing alloys. In a study by Sumitomo Metal Industries⁽²⁴⁾, the oxide growth in steam for

alloys T22 (2-1/4Cr-1Mo), T9, HCM9M, and the modified 9Cr-1Mo (T91) were compared based on 500 hr tests. Results showed the superiority of the T91 alloy over the other alloys. Masuyama *et al* compared alloys HCM12, HCM9M, 321H, and 347H in field tests in the temperature range 550 to 625°C (1020 to 1155°F) over a period of one year⁽²⁵⁾. Samples were inserted in the tertiary and secondary superheaters and reheaters. From the results, they concluded that the resistance to steam oxidation of HCM12 is superior to those of 321H and HCM9M and comparable to that of fine-grained 347H for exposure to the high-temperature region of the reheater. Subsequent monitoring over a period of three years has borne out their earlier conclusions⁽²⁶⁾. In addition to the inherent resistance of HCM12M steel to steam-side oxidation, Masuyama *et al* suggest that the tendency toward exfoliation of oxide scale would also be less for this alloy than for austenitic steels^(25,26). Additional improvements in 9 to 12% Cr steels may be possible by extending the chromizing^(27,28) and chromate conversion treatments⁽²⁹⁾ that currently are applied to lower-alloy steels, grain refinement during heat treatment has been shown to be clearly beneficial as well. Internal shot blasting is also known to improve the steam oxidation resistance of 300 series stainless steels by enhancing chromium diffusion. It is therefore anticipated that these steels would be used in the fine-grain and shot-peened conditions. Results of steam oxidation tests at 650°C (1200°F) for times up to 2000 h have been reported for several austenitic steels⁽³⁰⁾.

2.5.4 Summary of Tube-Material Status

Based on the discussion so far recommendations for materials selection have been made in Table 2-3. For phase 0 steam conditions, alloys T91, HCM12M, and AISI type 304 stainless steel are viable candidates for superheater and reheater tubing, provided that fire-side corrosion is not a major problem. Under mildly corrosive conditions, 310NbN stainless steel may be the most cost-effective option. For severe corrosion cladding, SS304 with IN72 (44%Cr) is recommended.

For intermediate-temperature applications corresponding to phase 1 steam conditions (595°C, or 1100°F), Tempaloy A-1 and type 347 fine-grained stainless steel are deemed to be adequate in the absence of corrosive conditions. Under mildly corrosive conditions, 310NbN stainless steel may offer the best combinations of creep strength and corrosion resistance. For severe corrosion, cladding with IN72 is recommended.

For phase 1B i.e. 620°C (593°C metal temperature) conditions Super 304H, Tempaloy AA1, Esshete 1250 and 17-14 CuMo may be acceptable under non-corrosive conditions. For mildly corrosive conditions alloys with 20-25% Cr such as HR3C, and NF709 will have the best combination of creep strength and corrosion resistance. For severe corrosion, cladding with IN72 is again recommended.

For the highest-temperature application corresponding to phase 2 steam conditions (650/650°C, or 1200/1200°F), the creep strength requirements are met by Inconel 617, 17-14 CuMo steel, Esshete 1250 and NF709. Among these alloys, 17-14 CuMo steel and Esshete 1250 have inadequate corrosion resistance and will have to be clad with corrosion-resistant claddings of Inconel 671 if corrosive conditions are present. NF709 and CR30A may be used without any

corrosion protection for mildly corrosive conditions, but will require cladding with IN72 for severely corrosive conditions..

2.6 Choice of Materials for Waterwalls

2.6.1 Metal Temperature Concerns

This issue has been discussed recently by Blum⁽³¹⁾. In boilers operating at 625°C/32 MPa, maximum midwall temperatures can be as high as 500-525°C, depending on magnetite deposits at the inside of the tube. This means that the creep resistance of standard low alloy ferritic steels such as T-11 is not adequate. Originally T-91 steel was the only suitable substitute. Under the COST program⁽³²⁾ it was demonstrated that this material can be fabricated into waterwalls. However a postweld heat treatment is required, which is difficult to do in the field. Two steels containing 2.5 and 12Cr% respectively developed by Sumitomo and MHI are more promising in that they do not require preheat or postweld heat treatment.^(31,33) Both steels have creep strength in the same range as T-91 and use similar precipitation strengthening mechanisms. Especially the 2.5%Cr steel appears promising for this application. It also has recently been approved by the ASME boiler code committee as T-23. Test panels are now in service in various boilers.

2.6.2 Waterwall Corrosion Concerns

Recent reductions in NO_x emissions, mandated by the Environmental Protection Agency in the USA have led to the introduction of deeply staged combustion systems, in which the air/fuel ratio is significantly less than 1, and additional combustion air is added above the burners via overfire air ports. Several boilers in the USA retrofitted with such systems have reported severe corrosion of low alloy steel waterwalls, with metal losses in the 1-3 mm/yr (40-120 mil/yr) range. Supercritical units are generally more severely affected than subcritical units and severe corrosion is generally limited to coals with more than 1%S. However above 1%S there is no strict correlation between S and corrosion rate. The highest corrosion losses are found in regions where H₂S rich substoichiometric flue gas mixes with air from the overfire air ports. Laboratory studies indicate that the high corrosion rates cannot be explained by the presence of H₂S and CO in the flue gas alone. Work by Kung⁽³⁴⁾ has shown that corrosion rates in gas mixtures, actually found in boilers, containing 500-1500 pm H₂S and 5-10% CO, are generally less than 0.5 mm/yr (20 mils/yr) at 450°C. More recently it was shown that the presence of FeS deposits can greatly increase the corrosion rate, but only under alternating oxidizing/reducing conditions or oxidizing conditions alone. Figure 2-15 shows corrosion losses of a low alloy steel, T-91 and SS-304 in the presence of FeS containing deposits and a gas mixture containing 1% oxygen. Although the corrosion rates are probably artificially high, because of the short duration of the test, it is clearly demonstrated that low alloy steels will corrode quite rapidly in the presence of FeS deposits and an oxidizing gas. The tests further show that claddings or weld overlays containing at least 18 and preferably more than 20% Cr are needed to assure acceptably low corrosion rates.

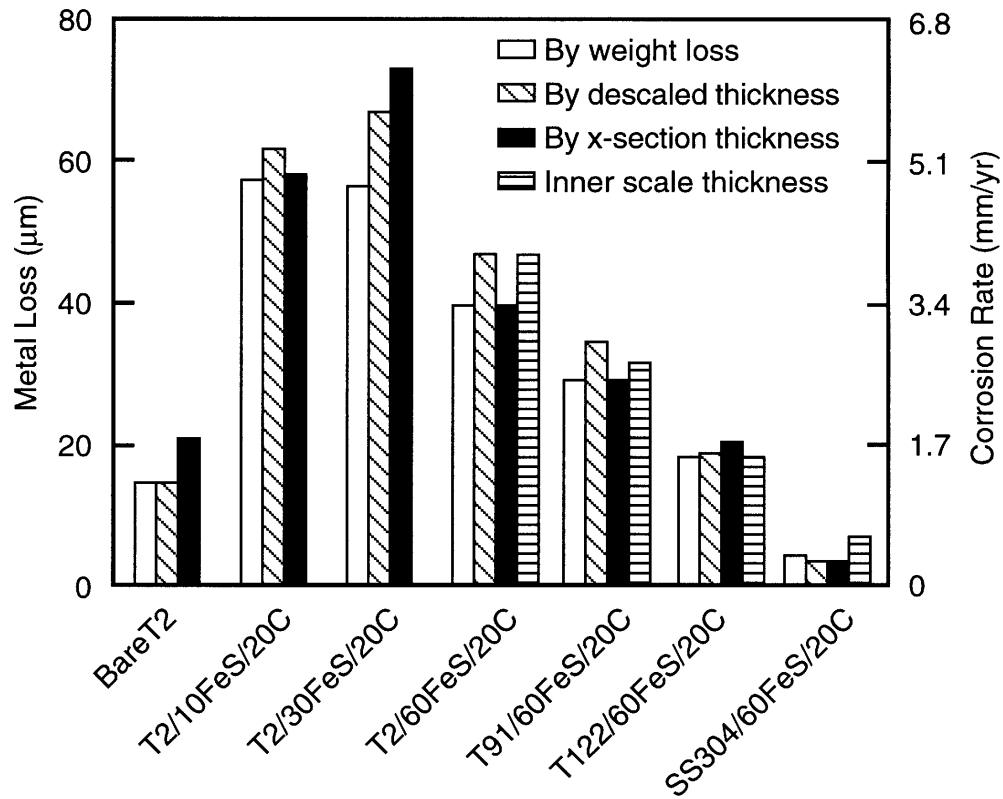


Figure 2-15
Corrosion of steels containing 0.5-18% Cr under FeS containing deposits in oxidizing flue gas

3

STEAM TURBINE MATERIALS

Candidate materials for use in steam turbines of advanced supercritical plants are listed in Table 3-1. The rationale behind these selections on a component specific basis is described in the following sections.

Table 3-1
Candidate Materials for Advanced Steam Turbines

Phase 0	31MPa (4500 psi) 565/565/565°C 1050/1050/1050°F	31MPa (4500 psi) 593/593/593°C 1100/1100/1100°F	31MPa (4500 psi) 620/620/620°C 1150/1150/1150°F	34.5MPa (5000 psi) 650/650/650°C 1200/1200/1200°F
HP/IP Rotor	Forgings of steels CrMoV or 12%Cr steels AISI 422 SS TOS 101 GE-original	12%Cr steel forgings of TR1100 X12CrMoVWNbN101-1 TOS107 GE-modified steel	12%Cr steel forgings of X18CrMoVNB91 TOS 110 EPDC Alloy B TR1200 HR1200	12%Cr steel HR1200 forging
Blade	AISI 422 SS 12Cr1Mo1WV (Westinghouse) 11Cr1MoVNBn (GE original)	TOS 202 GE modified steel	TOS 203 Candidate steel D (EPDC) Candidate steel C (EPDC)	M252 Refractalloy 26 Nimonic 90 Inco 718
Bolting	CrMoV AISI 422 SS Refractalloy 26	M252 Refractalloy 26	Nimonic 80 Inco X 750 Refractalloy 26	Nimonic 80 Refractalloy 26
Inner cylinder	CrMo steel (cast)	9%Cr steel cast	Advanced 9- 12%Cr steel (cast) Similar to P92, P122, E911	316 austenitic stainless steel
Nozzle box	“	“	“	“

3.1 HP/IP Rotors

The most important material properties for this application are creep strength, low cycle fatigue strength and fracture toughness. High creep strength is required to resist deformation and crack initiation in the bore or in the blade attachment areas. The low cycle fatigue strength is required to prevent cracking from thermal stresses due to cycling. The fracture toughness is needed to

contain the possibility of brittle fracture during transient conditions, i.e., startup/shutdown. Ferritic steels are invariably preferred to the austenitic steels to minimize risk of thermal fatigue.

The variety of compositions that have been explored in order to improve the creep strength are listed in Table 3-2. The workhorse steel of the industry for conventional power plants operating up to 545°C (1012°F)^{*} has been the 1%Cr 1%Mo 0.25%V steel. At higher temperatures 12%Cr steels are needed for creep strength as well as for corrosion resistance. The evolution of rotor steels has followed a path very similar to that of the boiler steel, as shown in Figure 3-1. The earliest 12%Cr steels have been the 12CrMoV steel X21CrMoV 121, capable of operation up to about 560°C (1040°F)⁽³⁵⁾. The next stage of development consisted of adding Nb + N or Ta + N or W resulting in three alternate versions of the 12 Cr steel. The Ta + N version was used in Japan; the Nb + N version was used by the General Electric Company; and the W added steels 12CrMoVW were used by the Westinghouse Electric Corporation in the USA⁽³⁶⁾. This class of steels gave an advantage of another 15°C (27°F) over the conventional 12CrMoV steel, but nevertheless were successfully exploited only up to 565°C (1050°F). Nb and Ta contribute to precipitation strengthening by formation of carbonitrides.

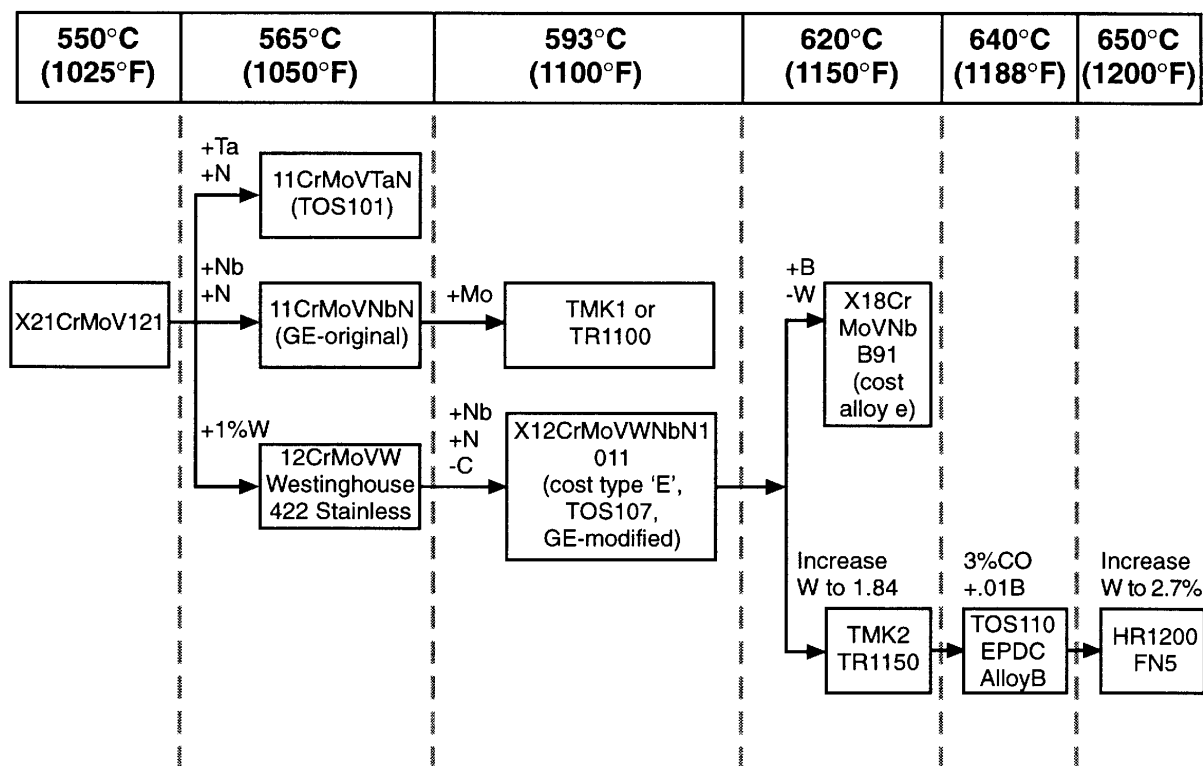


Figure 3-1
Evolution of HP/IP steam turbine rotor alloy showing compositional changes and increasing temperature capability

The next major development in the 80s consisted of adding W to the Nb-N or Ta-N steel to improve the solid solution strength. This resulted in the development of TOS 107 in Japan⁽⁴⁰⁾

^{*} All temperatures are metal temperatures.

(also referred to as General Electric modified in Ref. 37) and X12CrMoVWNbN 101-1 steel (E-type) in Europe under the COST 501 project⁽¹⁾. These alloys increased the permissible operating temperatures to 593°C (1100°F). An alternate route of increasing the Mo content to 1.5% from 1% and reducing the carbon content was claimed to have resulted in equivalent properties at 593°C (1100°F), due to solid solution strengthening of Mo and its ability to stabilize M_6C and $M_{23}C_6$ carbides^(38,39). This higher Mo alloy TMK1 or TR1100 entirely resembles the previous class of steels and the alleged superior properties are inadequately documented.

Further improvements to the X12CrMoVWNbN alloys were made by two routes. In the European COST 501 research, B additions, even in the absence of W were found to lead to superior creep properties with required creep strength up to 620°C (1150°F)⁽¹⁾. This alloy was named X 18CrMoVNbB91. The Japanese researchers on the otherhand, achieved higher creep strength by further increasing the W content to 1.8% from 1% resulting in alloy TMK2 (TR 1150).

The next stage of alloy modification involved further increasing the W content from 1.8 to 2.7% and adding 3%Co and 0.01B. This resulted in alloys HR 1200⁽⁴³⁾ and FN5⁽¹⁾ which are potentially capable of operation up to 650°C. Trial rotors have been made and properties evaluated for all the alloys described above including HR 1200. At the time of this writing, no trial rotor data have been reported for the composition FN5. The limiting temperature for the alloy is generally based on a design criterion of 10^5 hr rupture life at 125 MPa.

Stress rupture data representative of each class of steels is presented using the Larson-Miller parametric approach in Figure 3-2. CrMoV and X 21CrMoV 121 rotors have been in service and considerable long time data is available. CrMoV(Ta)NbN type rotors have also been in service since 1973. Toshiba reports introduction of TOS 101 in the year 1973 and nearly 20 rotors are currently in service⁽⁴⁰⁾.

With respect to the tungsten containing CrMoVWNbN steels, TOS 107 was first introduced in service in 1991⁽⁴⁰⁾. Currently there are about 10 rotors in 565°C steam turbine service⁽⁴⁰⁾. About 5 pilot rotors containing variants of similar steels such as X12CrMoVWNbN1011 have been introduced in service in the late 90s in Europe⁽¹⁾. Creep rupture data up to 80,000 hours have been collected. Numerous gas turbine disks of the alloy X12CrMoVWNbN 101 alloy also known as COST 501 E-type alloy have been placed in operation⁽¹⁾.

Trial rotor forging manufacture have been reported on alloy X18CrMoNbB91⁽⁴⁴⁾, TOS 110⁽⁴⁰⁾ and HR 1200⁽⁴³⁾. While Larson-Miller extrapolations suggest that these steels can be used at 620, 630 and 650°C respectively, the extent of long time creep data available is not clear. This is often a problem since, long time data are not obtained or not published due to commercial reasons and the validity of the parametric extrapolations cannot be independently verified. Furthermore, very few publications report creep rupture ductility values. Susceptibility to notch sensitivity is therefore not clear.

Fracture toughness data on various rotor steels have not been reported in detail. It has generally been asserted that the toughness of the new steels are at least as good or better than that of the 1CrMoV steels. An example of the type of comparisons offered is shown in Figure 3-3⁽¹⁾.

Earlier results published in Ref. 9 also confirm that the fracture toughness of the 12Cr steels are invariably better than that of conventional CrMoV steel.

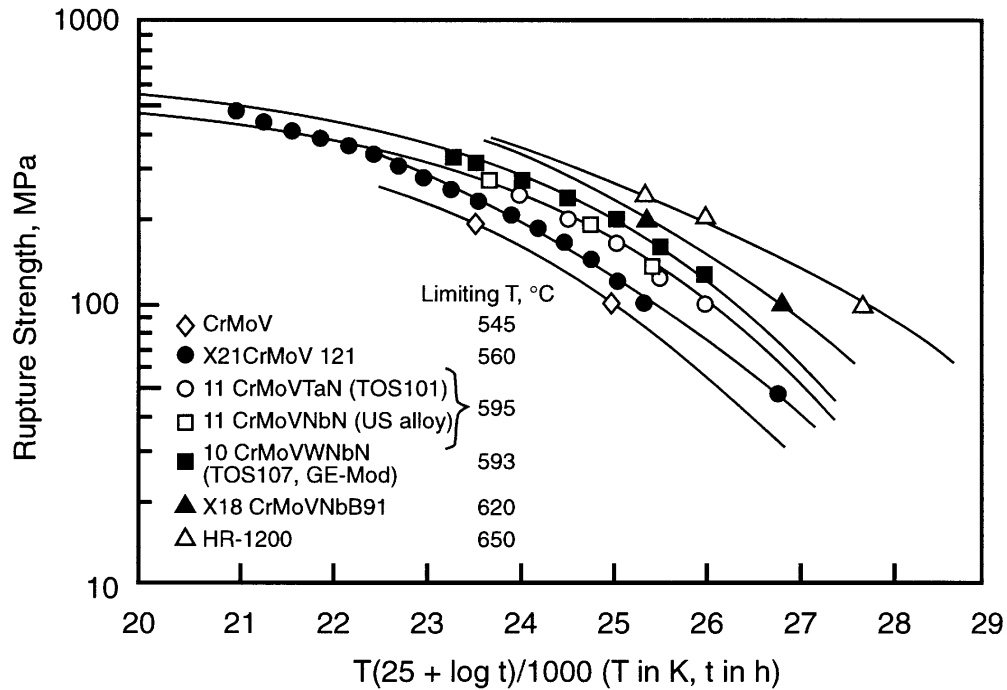


Figure 3-2

Larson-Miller rupture curves for commercial and developmental 12% Cr rotor steels

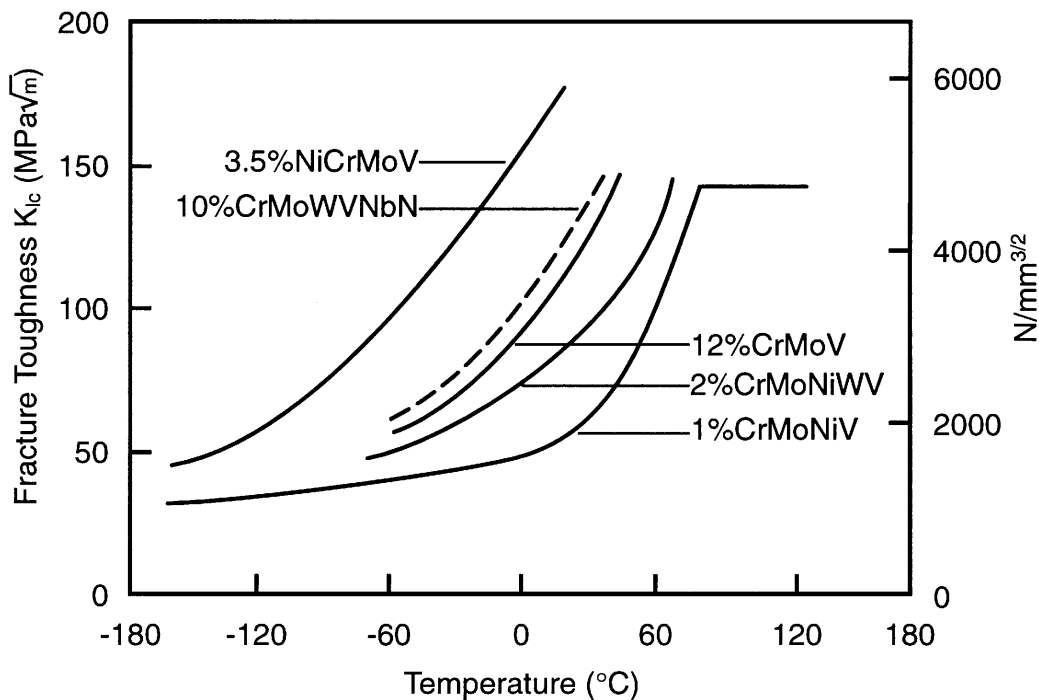


Figure 3-3

Fracture toughness of turbine rotor steels (1)

Table 3-2
Nominal Chemical Compositions of Candidate Alloys for High Temperature Rotors

Alloy Designation	C	Mn	Si	Ni	Cr	Mo	V	Nb	Ta	N	W	B	Co	Change	Limiting Steam T°C(°F)
X21CrMoV 121 ⁽¹⁾ (same as Alloy 13 ⁽¹⁾)	0.23	0.55	-	0.55	11.7	1.0	0.30								560 (1040)
11CrMoV TaN ⁽³⁵⁾ (same as Alloy 17, TOS101)	0.17	0.60		0.35	10.6	1.0	0.22		0.07	0.05					575 (1070)
GE – Original ^{(36) (37)} (same as Alloy 16) ⁽³⁵⁾	0.19	0.50	0.30	0.50	10.5	1.0	0.20	0.08 5		0.06					
11CrMoV NbN ⁽³⁵⁾ (same as Alloy 15) ⁽³⁵⁾	0.16	0.62		0.38	11.1	1.0	0.22	0.57		0.05					
Westinghouse ⁽³⁶⁾ (same as AISI 422)	0.23	0.80	0.40	0.75	13.0	1.0	0.25				1.0				
10CrMoV NbN (same as TMK1 ⁽³⁶⁾ , and TR(1100) ⁽³⁹⁾)	0.14	0.50	0.05	0.60	10.2	1.5	0.17	0.06		0.04					593 (1100)
TMK2 (TR115 0) ^(38,39,40)	0.13	0.50	0.05	0.70	10.2	0.40	0.17	0.06		0.05	1.8				620 (1150)
X18CrMoVNb B91 ^{(1) (44)} (also Type B2, alloy e) ⁽¹⁾	0.18	0.07	0.06	0.12	9.0	1.5	0.25	0.05		0.02		0.10			
TR1200 ⁽³⁶⁾	0.12	0.50	0.05	0.8	11.2	0.3	0.20	0.08		0.06	1.8				
TOS 110 ⁽⁴⁰⁾ (EPDC Alloy B) ⁽⁴¹⁾	0.11	0.08	0.1	0.20	10.0	0.7	0.20	0.05		0.02	1.8	0.01	3.0		630 (1166)
HR1200 ⁽⁴³⁾ (same as FN5) ⁽¹⁾	0.10	0.55	0.06	0.50	11.0	0.23	0.22	0.07		0.02	2.7	0.02	2.7		650 (1200)

The designations Alloy 15, 16, 17, etc. pertain to developmental alloys described in Ref. 35.

4

BLADE MATERIALS

Turbines designed to operate at the advanced steam conditions require advanced blade* material for the control stage and first stages of the reheat sections. Type 422 stainless steel has been successfully used up to 550°C (1025°F) in the past. Higher strength alloys are needed at higher temperature applications.

Ferritic 9-12%Cr alloys offer the major advantage that their thermal expansion coefficients closely match that of the 9-12%Cr rotors, so that no design modifications are needed to allow for differential expansion, such as may occur with the use of superalloy buckets. Many of the rotor alloys listed in Table 3-2 may meet the requirements for the advanced steam conditions, but there is little published data relating to their evaluations for use in blades. Muramatsu has suggested two ferritic alloys, Alloy C and Alloy D as candidate steels, for use up to 630°C (1166°F)⁽⁵⁾. Alloy C very closely resembles HR 1200 (also FN5 of Ref. 1) listed in Table 3-2. Candidate Alloy D contains less Co, but has a rhenium addition of 0.2%. Alloy D is nearly identical with what Toshiba refers to as TOS203⁽⁴⁰⁾. The compositions of these ferritic steels are listed in Table 4-1.

Superalloy materials offer an alternative to the advanced 12Cr material for application to the blades for the control stage and first reheat stages. Although superalloys have been used extensively in gas turbine applications, the adequacy of these alloys for steam turbine application needs to be evaluated.

In the early 90's, an EPRI project was undertaken to review available data on superalloy materials, and to select the most promising alloy for application to steam turbine blades.⁽⁴⁵⁾ Material data and other information obtained was documented in order to support the selection of the material. A tenon peening procedure was then developed for the selected superalloy.

The first step in the selection process was to investigate the most important material properties for blades designed for application at high temperatures. These properties were creep rupture strength, thermal expansion coefficient, and ductility.

* The terminology blade or bucket is used to denote the same part by different manufacturers.

Blade Materials

Table 4-1
Nominal Chemical Compositions of Candidate Alloys for Buckets (WT%)

Alloys	Fe	Ni	Co	Cr	Al	Ti	Mo	W	Nb	B	Zr	C	Mn	Si	Others	Ref.
M-252		Bal.	10.0	20.0	1.0	2.6	10.0			0.005		0.15	0.5	0.5		(1)
Inconel 718	18.5	Bal.		18.6	0.4	0.9	3.1		5.0			0.04	0.2	0.3		(1)
Refractaloy 26	16.0	Bal.	20.0	18.0	0.2	2.6	3.2					0.03	0.8	1.0		(1)
Nimonic 90		Bal.	16.5	19.5	1.45	2.45				0.003	0.06	0.07	0.3	0.3		(1)
HR 1200 (FN5) ⁽¹⁾ Alloy C ⁽⁵⁾	Bal.	0.5	2.7	11.0			0.23	2.7	0.07	0.02		0.10	0.55	0.06	V 0.22	
Alloy D ⁽⁵⁾ (T0S203) ⁽⁴⁰⁾		0.6	1.0	10.5			0.10	2.5	0.10	0.01		0.11	0.5	0.05	V 0.2 N 0.03 Re 0.2	

Most of the Ni-based superalloys have adequate creep rupture strength superior to the 12%Cr alloys. Ideally, the thermal expansion coefficient of the bucket alloy should be the same as that of the 12Cr turbine rotor. However, the thermal expansion coefficients of superalloys are generally greater than that of 12Cr steel. Therefore, as a first step selection, candidate superalloys were limited to those having thermal expansion coefficients close to that of 12Cr. This criterion limited candidate superalloys to those having mean thermal expansion coefficients less than $15 \times 10^{-6}/^{\circ}\text{C}$ ($8.3 \times 10^{-6}/^{\circ}\text{F}$), which resulted in a thermal expansion coefficient ratio between the bucket and rotor of less than 1.2.

A total of 16 superalloys were initially identified as potential candidates. The alloys were compared and rated in terms of acceptability on the basis of tensile strength, creep strength, notchbar creep strength, thermal expansion and peening capability. Based on the comparison, the selection was narrowed to 4 materials, i.e., M-252, Refractalloy 26, Nimonic 90 and Inconel 718. The composition of these alloys is provided in Table 4-1. A comparison of the stress rupture properties is shown in Figure 4-1.

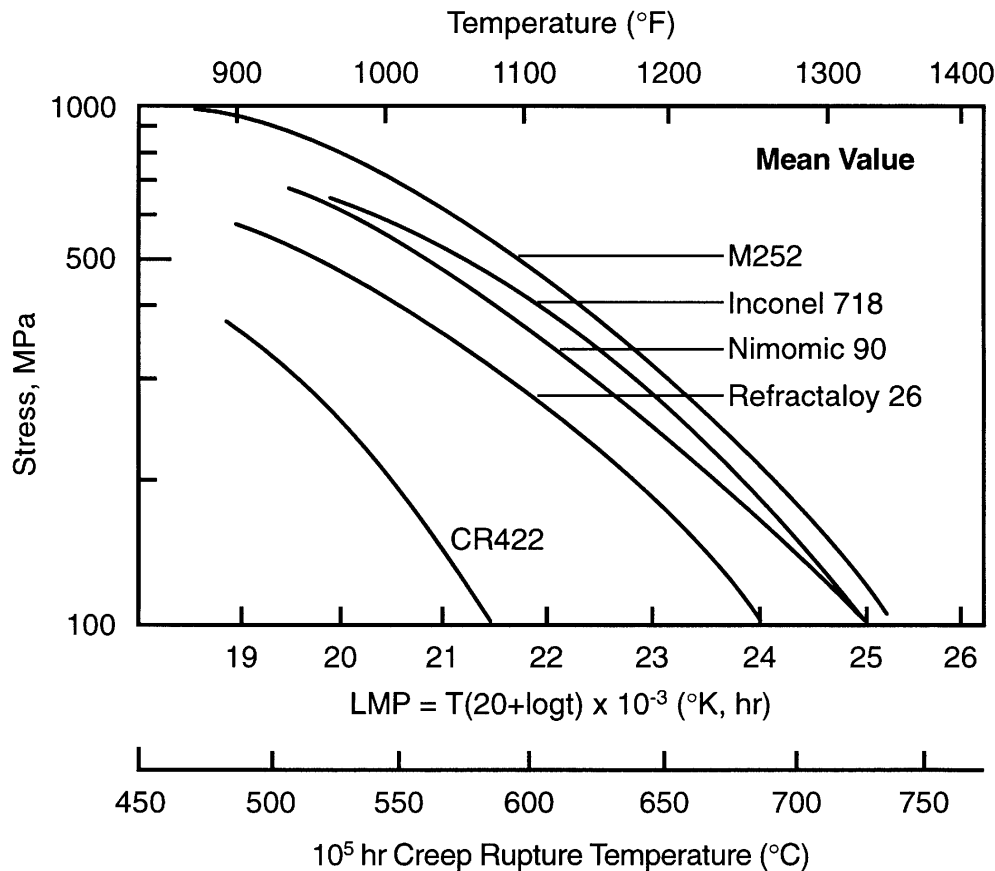


Figure 4-1
Stress rupture properties of candidate super alloys for bucket (based on Ref. 45)

Blade Materials

M-252 has had considerable favorable gas turbine experience in both manufacture and service exposure, and numerous blade sets have been in satisfactory service for 100,000 hours or more. This alloy has a low thermal expansion coefficient and shows a good balance of strength, ductility, and creep rupture strength. However, because there is structurally no requirement for tenon peening in gas turbine designs, there is no experience with peening operations concerning M-252.

Refractalloy 26 shows a good balance between strength and ductility, and good results were obtained in a preliminary test on tenon peening capability. Furthermore, Refractalloy 26 has been applied with good results in steam turbine blades in the research and development of an advanced steam turbine plant in Japan.

Nimonic 90 shows a relatively good balance in the investigated physical and mechanical properties. The manufacturing experience and the tenon peening capability are not clear. However, because the ductility of Nimonic 90 at room temperature is superior to that of Nimonic 80A, which has good tenon peening capability, tenon peening of Nimonic 90 may be successfully accomplished.

Inconel 718 exhibits very high tensile and yield strengths at room temperature, and there remains a high uncertainty concerning its tenon peening capability. Nevertheless, because this alloy has been utilized extensively in gas turbines for a variety of applications, it is difficult to exclude this alloy from the candidate alloys.

Table 4-2 summarizes the features and problems for the application of the four alloys (M-252, Refractalloy 26, Nimonic 90, and Inconel 718) selected above from the total candidate list of sixteen. These four alloys are potentially suitable for the blade application based upon the above results. M-252 and Refractalloy 26 are particularly favorable and are the selected candidates for the prime alloy and backup alloy, respectively.

The primary reason for the selection of M-252 as the prime alloy is because of the vast amount of favorable gas turbine experience. Its peening capability however was found to be much lower compared to Refractalloy 26. The reasons for the selection of Refractalloy 26 as the backup alloy are as follows: (1) it contains an alloy addition of iron and, therefore, represents an alternate choice to the exclusively nickel-based superalloys, (2) it shows a good balance of material properties, (3) it has a confirmed good peening capability, and (4) although it does not have extensive service history, it has performed well in the steam turbine blades in the research and development of an advanced steam turbine plant in Japan, which operated for about one year at 1200°F (649°C).

Refractalloy 26 has been used extensively and successfully in steam turbines over 30 years. Refractalloy 26 has been used not only for blades, but also for bolts and occasionally for rotors. The excellent properties of this alloy cited by Yamada *et al.*⁽⁴⁵⁾ and its vast operating experience make it a most desirable high temperature material.

Table 4-2
Features and Problems of Four Candidate Alloys for Blades

	Features and Problems
M-252	<ul style="list-style-type: none">• Extensive service history as gas turbine buckets• Good balance of strength and ductility• Lower thermal expansion coefficient• No tenon peening experience
Refractaloy 26	<ul style="list-style-type: none">• Experiences as advanced steam turbine buckets• Good balance of strength and ductility• Tenon peening experience
Nimonic 90	<ul style="list-style-type: none">• Good balance of strength and ductility• Tenon peening is hopeful (no experience)• Notch ductility behavior is not clear
Inconel 718	<ul style="list-style-type: none">• Extensive service history as gas turbine parts• No tenon peening experience

5

BOLTING MATERIALS

Considerations affecting the selection of high temperature bolting materials are nearly identical to those applicable to bucket materials. Bolting material must possess high temperature mechanical strength, creep strength, freedom from notch sensibility, resistance to stress relaxation (i.e. high creep resistance) and a coefficient of thermal expansion compatible with the 9-12%Cr ferritic steel casings. A major design consideration is to ensure that bolt will remain tight between scheduled outages, ranging from 20,000 to 50,000 hr.

In an EPRI-sponsored project, Mayer investigated worldwide experience on steam turbine bolt materials.⁽⁴⁶⁾ The chemical composition and service experience of four superalloys are shown in Tables 5-1 and 5-2. From Table 5-2, the failure rate of Incoloy 901 seems to be unacceptably high and the experience base with INCO X 750 seems too small. From among the other 3 promising alloys, Mayer chose Nimonic 80 and Refractalloy 26 for more detailed investigations.⁽⁴⁷⁾ They concluded that Nimonic 80A with some bolt design modifications was the best course to take. Seth however concludes that Refractalloy 26 should be preferred in the light of extensive service experience with the alloy⁽³⁷⁾.

Table 5-1
Chemical Composition of Superalloy Bolt Materials in Steam Turbines (37), (46)

	Chemical composition in %								
Alloy	C	Cr	Ni	Co	Mo	Ti	Al	B	Fe
Incoloy 901 ⁽¹⁾	Max. 0.10	11-14	40-45	Max. 1.0	5.0-7.0	2.0-3.0	Max. 0.35	0.010- 0.020	Bal.
Refractalloy 26	Max. 0.08	16-20	35-39	18-22	2.5-3.5	2.5-3.5	Max. 0.25	0.001- 0.01	Bal.
Inconel X750 ⁽¹⁾	Max. 0.08	14-17	Bal.	-	-	2.25- 2.75	0.4-1.0	(0.7- 1.2Nb)	5-9
PER 2B ⁽²⁾	Max. 0.15	19-23	Bal.	13-20	-	1.6-3	1-2	-	Max. 10.0
Nimonic 80A ⁽³⁾	Max. 0.10	18-21	Bal.	Max. 2.0	-	1.8-2.7	1.0-1.8	Max. 0.008	Max. 3.0

(1) trade name of INCO

(2) trade name of Aubert & Duval

(3) trade name of Wiggins Alloys

Bolting Materials

Table 5-2
Failure of Superalloy Bolt Materials in Steam Turbines (37), (46)

Bolt Material	No. of Units	No. of bolts	No. of failure cases	Percentage of failed bolts
Incoloy 901	49	434	15	14.9
Refractaloy 26	26	Abt. 50 000	?	Abt. 0.03
PER 2B	6	1470	0	0
Nimonic 80A	231	20 291	24	0.37
Inconel X750	3	28	1	3.5

6

CONCLUSIONS

1. The materials technology needed to construct ultra supercritical plants with steam temperatures up to 625°C and pressure up to 34 MPa is largely available mostly in the form of commercial, code approved steels.
2. For heavy section piping and headers, the widely accepted P91 steel will suffice for use up to 593°C. Three new ferritic steels, NF616 (P22), HCM12A (P122) and E911 have been developed and have been shown to be capable of operation up to 620°C. These steels are code approved and are being widely utilized in field trials. Two steels, NF12 and SAVE12, capable of operating up to 650°C have emerged, but are still in a developmental stage. Concern with oxidation may limit the use of these steels to 620°C.
3. For superheater/reheater applications ferritic steels will be possible for sections operating below 593°C (1100°F) metal temperature (i.e., 565°C (1050°F steam), provided corrosion is not an issue. However, they are not widely used. Under more corrosive conditions and for all conditions exceeding metal temperature of 593°C (1100°F), austenitic stainless steels will have to be used. For non corrosive conditions, steels and alloys with a high creep strength, but relatively low Cr content are adequate. Examples are: 17-14 CuMo or super 304H. For mildly corrosive conditions, alloys with 20 and preferably 25% Cr, such as 310NbN (HR3C) or NF709 should provide satisfactory performance. For highly corrosive conditions, high strength alloys, clad or weld overlayed with alloys such as IN671 or IN72 (44-50%Cr) must be used.
4. The concern about weldable high strength waterwall materials has been eliminated with the introduction of HCM2S (T23) and HCM12 steels. HCM12 was preferred over HCM12A because of its higher weldability. More field experience, however, is needed to confirm their suitability.
5. Corrosion of waterwalls of supercritical boilers may be a problem for some fuels and low NOx combustion systems. It is expected that coating or cladding with alloys containing more than 20% Cr will be required. This issue is being intensively investigated in the USA at present.
6. For HP/IP steam turbine rotors, several alloys, TMK1, TR1100, TOS107 and a modified GE alloy can operate up to 593°C. Some European alloys and Japanese alloys (TOS110, EPDC Alloy B) have been tested as trial rotors and can be used up to 620°C. For 650°C application alloys HR1200 and a European alloy designated FN5 seem to be promising candidates, but have not yet been fully qualified.

Conclusions

7. Many of the rotor type ferritic alloys also appear suitable for control stage blading up to 620°C. Superalloys M-252 and Refractalloy 26 seem to be the leading candidates for use up to 650°C.
8. For high temperature bolting, Nimonic 80A and Refractalloy 26 seem to be the most promising.

7

REFERENCES

1. D.V. Thornton and K.H. Meyer, "European High Temperature Materials Development" in Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J.W. Nutting, Ed.; IOM Communications Ltd., London, pp 349-365, 1999.
2. K.H. Mayer *et al*, "New Materials for Improving the Efficiency of Fossil-fired Thermal Power Stations", International Joint Power Generation Conference, PWR-Vol. 33, ASME, 1998, pp 831-841.
3. R.D. Hottenstine, N.A. Phillips and R.A. Dill, "Development Plans for Advanced Fossil Fuel Power Plants", Report CS-4029, EPRI, Palo Alto, 1985.
4. M. Gold and R.I. Jaffee, "Materials for Advanced Steam Cycles", ASM J. of Materials for Energy Systems, Vol. 6 (No. 2), 1984, p 130-145.
5. K. Muramatsu, "Development of Ultra Supercritical Plant in Japan" in Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J.W. Nutting, Ed.; IOM Communications Ltd., London, pp 543-559, 1999.
6. W. Bendik *et al*, "New 9-12% Cr Steels for Boiler Tubes and Pipes: Operating Experiences and Future Developments", in Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J.W. Nutting, Ed.; IOM Communications Ltd., London, pp 133-142, 1999.
7. W.T. Bakker, "Materials for Advanced Boilers", in Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J.W. Nutting, Ed.; IOM Communications Ltd., London, pp 435-455, 1999.
8. F. Masuyama, "New Developments in Steels for Power Generation Boilers", in Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J.W. Nutting, Ed.; IOM Communications Ltd., London, pp 33-48, 1999.
- 8b. W. Garrison and R.F. Buck, "An Overview of the Development of Advanced 9-12% Cr Steels," In ASM Symposium on Materials for Rotating Machinery, Oct 1999, Cincinnati.
9. R. Viswanathan, "Damage Mechanisms and Life Assessment of High-Temperature Components", ASM International, Metals Park, OH, 1989.
10. H. Haneda *et al*, In Proceedings of the Third International Conference on Steel Rolling, Tokyo, September 2-6, 1985, pp 669-676.

References

11. T. Topoda *et al*, “Development of Thick Walled Pipes and Headers of Modified 9Cr Steel”, Proc. of the Second International Conference on Improved Coal-fired Power Plants, 2-7 Nov. 1988, Palo Alto, CA, EPRI Report GS-6422, pp 36-1.
12. B.W. Roberts *et al*, “Thick Section Welding of Modified 9Cr-1Mo (P91) Steel”, EPRI Report TR-101394, September 1992.
13. T. Fujita *et al*, “Development of a 9Cr Steel” in EPRI Report CS-5581-SR, p 5-201.
14. E. Metcalfe, Ed., Proc. “New Steels for Advanced Power Plants”, EPRI Report TR-104952, 1995.
15. F. Masuyama and F.T. Yokoyama, NF616 Fabrication Trials in Comparison with HCM12A, EPRI Report TR-104952, p 30, 1995.
16. K. Yoshikawa *et al*, *Therm. Nucl. Power*, Vol. 12 (No. 12), 1985, p 1325-1339.
17. F. Masuyama, H. Haneda and B.W. Roberts, “Update Survey and Evaluation of Materials for Improved Coal-Fired Power Plants”, Report CS-5181-SR, EPRI, Palo Alto, 1988, pp 5.85 to 5.108.
18. H. Teranishi *et al*, presented at the International Conference on High Temperature Alloys, Preprint Paper No. 21, Petten, The Netherlands, Oct 15-17, 1985.
19. T. Ikeshima, *Bull. Japan Inst. Metals*, Vol. 22 (No. 5), 1983, p 389.
20. Ohtomo *et al*, High Temperature Corrosion Characteristics of Superheater Tubes, Ishikawajima Harima Industries, *Engg. Rev.*, Vol. 16 (No. 4), Oct 1983.
21. A.L. Plumley and W.R. Rocznia, Coal Ash Corrosion Field Testing of Advanced Boiler Tube Materials, in *Proceedings of the Second International Conference on Improved Coal-Fired Power Plants*, Electric Power Research Institute, Palo Alto, CA, Nov 1-4, 1988.
22. A.F. Armor, R.I. Jaffee and R.D. Hottenstine, “Advanced Supercritical Power Plants – The EPRI Development program, Proc. of American Power Conference, Vol. 46, 1984, p 70.
23. J.L. Blough *et al*, “Superheater Corrosion – Field Test Results”, Report TR-103438, EPRI, Palo Alto, Nov 1993.
- 23a. J.L. Blough *et al*, “superheater Corrosion in Ultra Supercritical Power Plants, Long-Term Field Exposure at TVA’s Gallatin Plant”, EPRI Report TR-111239, EPRI, Palo Alto, 1999.
24. “Properties of Super 9Cr Steel Tube (ASTM) A 213-T 91,” Report 803 F-No. 1023, Sumitomo Metal Industries, July 1983.

25. F. Masuyama, H. Haneda, T. Daikoku, and T. Tsuchiya, "Development and Applications of a High Strength, 12% Cr Steel Tubing with Improved Weldability", Technical Review, Mitsubishi Heavy Industries, Ltd., Japan, Oct. 1986, p 229-237.
26. F. Masuyama, H. Haneda, K. Yoshikawa, and A. Iseda, Three Years of Experience with a New 12% Cr Steel in Superheater, in *Advanced in Materials Technology for Fossil Fuel Power Plants*, R. Viswanathan and R.I. Jaffee, Ed., American Society for Metals, Metals Park, OH, 1987, p 259-266.
27. A.J. Blazewicz and M. Gold, "Chromizing and Turbine Solid Particle Erosion", ASME Paper No. 78, JPGC PWR-7, Joint ASME/IEEE/ASCE Power Generation Conference, Dallas, September 1978.
28. P.L. Daniel *et al*, "Steamside Oxidation Resistance of Chromized Superheater Tubes", CORROSION 80, NACE Conference, Chicago, May 1980.
29. J.M. Rehn *et al*, "Controlling Steamside Exfoliation in Utility Boiler Superheaters and Reheaters", Paper No. 192, CORROSION 80, NACE Conference, Chicago, May 1980.
30. K. Kubo, S. Murase, M. Tamura, and T. Kanero, Application of Boiler Tubing Tempalloy Series to the Heat Exchanger of Advanced Coal-Fired Boilers, in *Proceedings of the First International Conference on Improved Coal-Fired Power Plants*, A.F. Armor, W.T. Bakker, R.I. Jaffee, and G. Touchton, Ed., Report CS-5581-SR, Electric Power Research Institute, Palo Alto, CA, 1988, p 5-237 to 5-254.
31. R. Blum, "Materials Development for Power Plants with Advanced Steam Parameters. Utility Point of View", *Proc. Materials for Advanced Power Eng.*, 1991, 3-6 Oct. 1994, Liege, Belgium, Kluwer Ac. Publ. Dordrecht, The Netherlands, 15.
32. C.J. Franklin and C. Henry, "Materials Development and Requirements for Advanced Boilers", Reference 31, 89.
33. F. Masuyama, Y. Sawaragi *et al*, "Development of a Tungsten Strengthened Low Alloy Steel with Improved Weldability", Reference 31, 173.
34. S.K. Kung, "Prediction of Corrosion Rate for Alloys Exposed to Reducing/Sulfidizing Combustion Gases", *Corrosion* 97, NACE 1997, 97-136.
35. D.L. Newhouse, "Guide to 12Cr Steels for High and Intermediate Pressure Turbine Rotors for the Advanced Coal-Fired Steam Plant", Report CS-5277, Electric Power Research Institute, Palo Alto, CA, 1987.
36. D.L. Newhouse *et al*, "A Modified 12%Cr Steel for Large High Temperature Steam turbine Rotors", Presented at ASTM 58th Annual Meeting, June 1965.

References

37. B. Seth, "U.S. Developments in Advanced Steam Turbine Materials" in Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J.W. Nutting, Ed; IOM Communications Ltd., London, pp 519-539, 1999.
38. T. Fujita, "Advanced High Cr Ferritic Steels for high Temperature", Met. Prog., August 1986, pp 33-40.
39. A. Hizume *et al*, "The Probability of a New 12%Cr Rotor Steel Applicable to Steam Temperature Above 593°C" in Advances In Materials Technology for Fossil Fuel Fire Plants, R. Viswanathan and R.I. Jaffee, Ed., American Society for Metals, Metals park, OH, 1987, pp 143-153.
40. M. Miyazaki, M. Yamada, Y. Tsuda and r. Ishii, Advanced Heat Resistant Steels for Steam Turbines, in same volume as Ref. 37, pp 574-595.
41. K. Muramatsu, "Development of Ultra-Supercritical Plant in Japan" same volume as Ref. 37, pp 543-559.
42. K.H. Schonfeld and H. Wagner, "Experience in Manufacturing and Mechanical Properties of Turbine Rotor Forgings and Discs in Improved 10% CrMoWVNbN Steel", same volume as Ref. 37, pp 375-385.
43. K. Midaka *et al*, "Development of Heat Resistant 12%CrWCoB Steel Rotor for USC Power Plant", same volume as Ref. 37, pp 418-429.
44. M. Maurischat *et al*, "Metallurgical Procedure and Results of Melting of Boron Alloyed 10wt%Cr ESR Steel for Power Generation Machinery", same volume as Ref. 37, pp 386-396.
45. Y. Yamada, A.M. Betran and G.P. Wozney, "New Materials for Advanced Steam Turbines, Vol. 1: Evaluation of Superalloys in Turbine Buckets, Report TR-100979, EPRI, 1992.
46. K.H. Mayer, "New Materials for Advanced Steam Turbines", Vol. 5, Survey of Superalloy Bolt Failures in High Temperature Service", TR-100979, Vol. 5, September 1992, EPRI, Palo Alto.
47. K.H. Mayer and H. Konig, "Relaxation and Creep of NiCr Bolting Alloys for Application in Steam Turbines of Coal-Fired Power Plants", TR-104846, February 1995, EPRI, Palo Alto.

